8-2006

Kinetics of sulfur and peroxide cured EPDM rubber aging in chloraminated water.

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KINETICS OF SULFUR AND PEROXIDE CURED EPDM RUBBER AGING IN CHLORAMINATED WATER

By

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B. Tech, S.V University College of Engineering, 2003

A thesis
Submitted to the Faculty of the
Graduate school of the University of Louisville
in Partial Fulfillment of the Requirements
for the Degree of

Master of Science

Department of Chemical Engineering
University of Louisville
Louisville, Kentucky

August 2006

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A Thesis Approved on

June 26, 2006

By the following Thesis Committee:

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(Thesis Director)

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DEDICATION

This thesis is dedicated to my parents

Mr. Muni Chandra Naidu Valleru

And

Mrs. Yasoda Valleru

who have given me invaluable educational opportunities.

ACKNOWLEDGEMENTS

I would like to sincerely thank my academic director, Dr. Thomas L Starr, for his guidance throughout my graduate study and thesis work. I would also like to express my gratitude to Mr. Mark Schreck for his support during the research work and my practical training at Hexion Specialty Chemicals. I immensely appreciate the direction and help of Dr. Thomas Rockaway and Dr. Gerold Willing for their invaluable suggestions and help with various aspects of research and results. I would also thank Ms. Rodica McCoy for helping me patiently in getting started with various instruments for my laboratory work.

Also, I would like to convey special thanks to Ranjith, for his understanding and patience during tough times; Rupa, for her endurance and a continuous support; Rajmohan for his valuable inputs and suggestions to my thesis work.

ABSTRACT

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Jahnavi Valleru

June 26, 2006

Elastomer degradation when exposed to chloraminated potable water is dependent on a number of poorly understood factors. Temperature and chloramine concentration are both believed to play roles, however, they have not been adequately defined. In order to estimate the material performance and predict the service life of elastomeric parts, knowledge of degradation modes, rate constants of the aging process and their activation energies is useful.

EPDM elastomers are used in numerous applications which require resistance to ozone attack and weather due to their stable, saturated polymer backbone structure. Accelerated aging experiments were conducted on both EPDM – S and EPDM – P at three concentration levels and temperatures. Tensile properties are used to study the extent of degradation through a 30-day aging period which are used to estimate the crosslink densities of both the materials. A rate expression is developed based on the rate of change in cross link densities. The rate constants are estimated and they are used to estimate the activation energies and frequency factors using an Arrhenius relationship.

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CHAPTER I

INTRODUCTION

All structural materials display a degree of elasticity, but elastomers as a materials class are distinct. They can be loosely defined as macromolecular in structure, stretchable under low stress to at least twice their original length, and having a high degree of shape memory. They have become indispensable to the manufacturing industry and in particular industry producing valves, pipes, fittings, and the host of appurtenances required by the water works field.

Since the early 1900s, water systems throughout the US have included disinfection in their purification process. Originally, free chlorine was used as the only disinfectant, however, due to regulatory, economic and health issues, many systems have switched to chloramines in the distribution system. The chloramine residual is generally preferred because of its persistence in the distribution system and its tendency to form fewer disinfection by-products. In some situations, however, chloramine residuals have had significant negative impacts on the elastomeric parts of water distribution infrastructure.

Elastomer degradation when exposed to potable water is dependent on a number of poorly understood factors. Simmons and Evanson (1988) conducted research that dealt directly with potential mechanisms of chloramine attack. They were able to demonstrate that the chloramine effects on the raw polymer were minimal and that the vulcanizate impact was substantial, including loss of tensile strength and extensive swelling. This was true for Nitrile, Butyl and EPDM based elastomers. They were also able to demonstrate

that the extent of attack was dependant on the form of the cross-linking; the more common sulfur based vulcanizates were more susceptible to attack than elastomers cured in a peroxide process.

To further investigate the impact of the vulcanization process on chloramine resistance, sulfur cured and peroxide cured EPDM materials are selected for failure analysis and degradation rate assessment. A background of EPDM rubber compounding and molecular structure is discussed in chapter 'Compounding of EPDM – S and EPDM – P'. These elastomers are subjected to accelerated aging in chloramine solutions at three concentration levels and three temperatures. The design and set-up of the accelerated tests are presented in the chapter 'Equipment and procedures'. Also, the operating procedure of Instron tensile testing machine which is used to measure the tensile properties is explained in this section.

Deterioration in tensile properties is measured at set intervals during a 30-day aging period. Tensile properties are used to determine the cross-link densities of both the materials. The rates of change are further analyzed to model degradation reaction kinetics and estimate the respective activation energies. In addition to a comparison of activation energies and reaction rates of EPDM – S and EPDM –P, the mode of failure is also discussed in the 'Performance results and discussion' chapter.

CHAPTER II

COMPOUNDING OF EPDM - S AND EPDM - P RUBBER

II.1 Nomenclature

Ethylene - propylene rubbers are random copolymers of the two hydrocarbons ethylene and propylene with the ethylene varying from 40% to 70% by weight. Small quantities of a third monomer are added to produce ethylene-propylene terpolymers which can be vulcanized in the usual way. EPDM follows a nomenclature convention endorsed by the American Society for Testing Materials and the International Standards Organization and applies to the more common, sulfur vulcanizable product which includes in the rubber molecule a minor percentage of a diene monomer in addition to ethylene and propylene. The basis for the letter designation, EPDM, is: Ethylene, Propylene, Diene and Methylene respectively. In this case, the methylene molecules are the repeating units (CH_2), or "Vertebrae", in the "Spine" of the polymer.

II.2 Polymer Structure

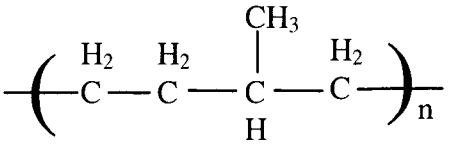
The structure of the regular, alternating amorphous copolymer of ethylene

$$H_2C = CH_2$$

and propylene

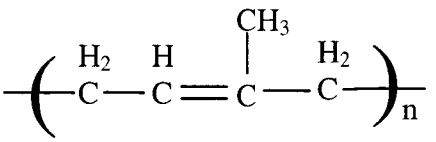
$$H_3C - \underset{H}{C} = CH_2$$

can be written as,



Ethylene Propylene

This structure is remarkably similar to the structure of natural rubber, *cis* 1, 4 polyisoprene:



It is not surprising; therefore, that the regular, alternating copolymer of ethylene and propylene is a decidedly rubbery material since its classical structure so closely approaches that of the first useful elastomer, natural rubber.

The equimolar structure of ethylene and propylene, as shown previously, is probably not achieved in the present commercial ethylene/propylene rubbers. The compositions of the commercial materials are generally given on a weight percentage basis. Although the rubbery properties of the ethylene/propylene copolymers are exhibited over a broad range of composition, the commercial products are generally in the weight percentage range of 50/50 or 75/25 ethylene/propylene.

II. 3 Polymer Unsaturation (EPDM):

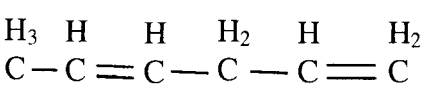
The structure of EPDM as illustrated previously shows this to be a saturated synthetic rubber. There are no double bonds in the polymer chain as there are in the case of natural rubber and in most common commercial synthetic rubbers (e.g., SBR, CPBR, NBR, etc.,). The main chain unsaturation in these latter materials introduces points of

weakness. When exposed to the degrading influences of light, heat, oxygen and ozone, the unsaturated rubbers tend to degrade through mechanisms of chain scission and crosslinking involving the points of carbon-carbon unsaturation. Since EPM does not contain any carbon-carbon unsaturation, it is inherently resistant to degradation by heat, light, oxygen and, in particular, ozone.

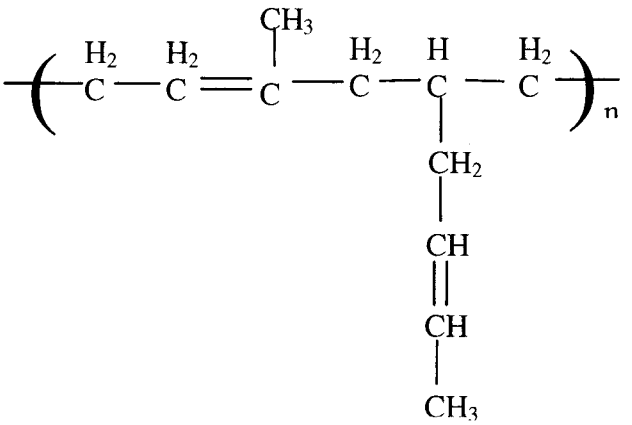
The double bonds in natural rubber and the common polydiene synthetics, aside from rendering these elastomers susceptible to environmental degradation, are essential to their curing into useful rubber products using conventional chemical accelerators and sulfur. The entire world's rubber industry is based on the vulcanization chemistry which was first demonstrated by Charles Goodyear in 1839 and involves carbon-carbon double bonds in a sulfur crosslinking reaction. EPM, a saturated elastomer, cannot be cured or crosslinked using the long-established manufacturing practices and chemicals pertinent to the unsaturated rubbers. A more commercially attractive product would be one which retained the outstanding performance features (e.g., heat, oxygen, ozone resistance) and which included some carbon-carbon unsaturation from a small amount of an appropriate diene monomer to accommodate it to conventional sulfur vulcanization chemistry.

II. 4 Diene monomers in EPDM:

Efforts to introduce one common diene monomers into the EPDM molecule have been unsuccessful. Searches for appropriate nonconjugated dienes resulted in the discovery of fifty such chemicals. The lowest molecular weight straight chain diolefin which meets the requirements is 1, 2 hexadiene:

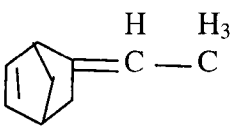


When this chemical is introduced with ethylene and propylene, the terminal double bond is active with respect to polymerization. The internal unsaturation is passive at this stage but remains in the resulting terpolymer as a substituent, or pendant, location for sulfur vulcanization:

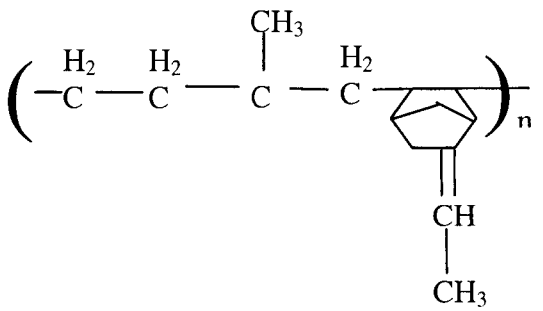


Ethylene propylene 1, 4 hexadiene

The resulting Ethylene/propylene/1, 4 hexadiene terpolymer (EPDM) is an important commercial material. Dicyclopentadiene is used in certain grades of EPDM which are made by a number of manufacturers. It enters the polymer readily with much higher polymerization efficiency than 1, 4 hexadiene. However, the most widely used diene in current commercial EPDM is ethylidene norbornene (ENB).



As with the other bridged ring dienes, ENB shows a high rate of polymerization through the double bond in the bridged ring. The substituent internal double bond is also very active with respect to sulfur crosslinking. The structure of EPDM containing ENB is,



The most common commercially used dienes in EPDM are 1, 4 hexadiene, dicyclopentadiene (DCPD) and ethylidene norbornene (ENB). These enter the polymer through the double bond which is more active in this function and leave the second double bond substituent or external to the polymer chain where it is then available to function in the classical chemistry of the sulfur vulcanization of rubber.

II. 5 Manufacturing Process of EPDM

II.5.1 Feed Specifications:

Ethylene is copolymerized by saturating the liquid reaction mixture with a given concentration of propylene and maintaining the saturation at this level throughout the reaction. The composition of the copolymer being formed can be maintained by monitoring the composition of the off-gas from the reaction and adjusting the ratios of the ethylene and propylene in the inlet streams.

When incorporating a diene such as dicyclopentadiene to give a curable polymer, all of the dicyclopentadiene may be present before the catalyst is added or alternatively, part or all of the dicyclopentadiene may be added during the copolymerization process. This introduction may be continuous or periodic during the reaction.

II.5.2 Temperature and Pressure:

The copolymerization reaction may be carried out over a wide range of temperatures. In general, as the temperature of the reaction increases, the catalyst life and the molecular weight of the copolymer decrease. Temperatures within the range of 0°C 25°C to about 80°C may be used. Pressures from 14 to 1,000 psig can be used. In the case of ethylene – propylene mixtures, the preferred polymerization pressures range from 50 to 200 psig.

II.5.3 Reaction Medium:

The copolymerization process is preferably carried out in an inert liquid organic diluent which is a solvent for the polymerization system. To obtain a co-polymer product of homogenous composition throughout, the diluent should be one that is a solvent not only for the monomers being copolymerized but also for the copolymer that is produced. In addition, it should also be a solvent for the catalyst so that the entire copolymerization reaction mixture is homogenous throughout the copolymerization process.

Suitable diluents for the copolymerization are, in general, the hydrocarbon solvents, i.e. aromatic, alicyclic and aliphatic hydrocarbons and chlorinated aromatic, alicyclic and aliphatic hydrocarbons and mixtures thereof. Examples of such diluents that may be used include hexane, heptane, octane, nonane, decane, benzene, toluene, methylene chloride, carbon tetrachloride tetrachloroethylene, chlorobenzene, dichlorobenzene etc.

II.5.4 Catalyst:

One of the criteria in carrying out the copolymerization process and producing a homogenous product of uniform composition and narrow molecular weight distribution is the catalyst that is used for the copolymerization reaction. It must, as a rule, be completely soluble in the reaction mixture.

A vanadium oxytrichloride, aluminum alkyl, iodine mixture is a useful catalyst. The catalyst systems are made by contacting vanadium tris (acetylacetonate) with selected organoaluminum compounds in the presence of selected liquid halogenated aliphatic hydrocarbons which serve as the reaction media when these catalyst systems are used to polymerize the monomers.

II.5.5 Product recovery:

The polymerization may be stopped by deactivating the catalyst with an alcohol such as isopropanol. The polymers formed are isolated by conventional filtration after the slurry has been processed. In general, the polymer is treated with an aqueous mineral acid to remove vanadium and aluminum salts; the solution or slurry is thereafter washed with distilled water until it is acid – free.

Improved catalyst removal may be attained by adding to the solution, as it recovered from the reactor, a surfactant, a chelating agent, and water, and then agitating the mixture in order to emulsify the solution. Once the emulsion has been formed, the gel will rise to the surface in a form resembling oatmeal, and may be readily removed by skimming or centrifuging. After removal of the gel, the emulsion is broken by heating to a temperature in excess of 65°C, preferably about 88°C, and the aqueous phase, containing dissolved catalyst residues, is separated from the hydrocarbon phase.

II.6 Sulfur Vulcanization

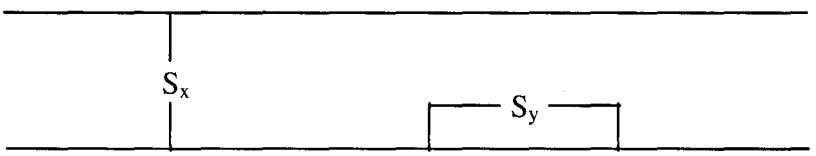
After the EPDM rubber compound has been properly mixed and shaped into blanks for molding, or calendered, extruded, or fabricated into a composite item, such as a tire, it must be vulcanized by one of many processes. During vulcanization, the following changes occur:

1. The long chains of the rubber molecules become crosslinked by reactions with the vulcanization agent to form three- dimensional structures. This reaction transforms the soft plastic – like material into a strong elastic product.

2. The rubber loses its tackiness and becomes insoluble in solvents and is more resistant to deterioration normally caused by heat, light and aging processes.

II.6.1 Mechanism:

Since EPDM rubber contains unsaturation, vulcanization with sulfur is possible, and it is in general the most common vulcanizing agent used. With sulfur, crosslinks and cyclic structures of the following type are formed:



Generally, x in an efficient accelerated curing system is about 1 or 2, with little or no cyclic groups formed. In inefficient systems x equals up to 8 and many cyclic structures are formed. The total amount of sulfur combined in these networks is usually called the "Coefficient of Vulcanization" and is defined as the parts of sulfur combined per one hundred parts of rubber by weight. For most rubbers, one crosslink for about each 200 monomer units in the chain is sufficient to produce a suitable vulcanized product. It is these amounts of cyclic sulfur (y) and the excessive sulfur in the crosslinks (x) which contribute to the poor aging properties of the vulcanizates.

Three agents essential to the sulfur vulcanization on EPDM are sulfur, a metal oxide, and a vulcanization accelerator. Of the metal oxides examined, only zinc and cadmium oxides are of practical significance. Zinc oxide is the preferred activator because it is more efficient, lower in cost, and less hazardous to use.

The best accelerators for the vulcanization of EPDM are also commonly used in natural rubber. However, their specific behavior differs from their response in rubber.

The relatively slower rate of vulcanization of EPDM requires a higher accelerator concentration, higher curing temperatures, or both. The most active accelerators include 2-mercaptobenzothiazole, thiuram sulfides, dithiocarbamates, and their simple derivatives. Of the three classes, the thiuram sulfides and dithiocarbamates are generally preferred because they produce rapid curing without scorching and do not over cure on long cure cycles. For many uses, however, 2-mercaptobenzothiazole and its derivatives, alone or in combination with thiurams or dithiocarbamates, provide adequate acceleration with processing safety.

EPDM polymers are amorphous and are similar to other non-crystallizing elastomers in the low tensile strength of their gum vulcanizates. However, high tensile strength is easily obtained by the incorporation of reinforcing fillers. The fillers commonly used in the rubber industry are carbon blacks, clay, calcium carbonates, calcium silicate, fine particle talcs and silicas. Carbon blacks are preferred for maximum reinforcement.

Vulcanization is normally accomplished by applying heat for a specified time at the desired level. The most common methods for vulcanization are carried out in their molds held closed by hydraulic presses and heated by contact with steam-heated platens, which are a part of the press in open steam in an autoclave, under water maintained at a pressure higher than that of saturated steam at the desired temperature, in air chambers in which hot air is circulated over the product, or by various combinations of these methods. The vast majority of products are sulfur-cured; that is, sulfur crosslinks join the rubber chains together as described above.

The time and temperature required for vulcanization of a particular product may be varied over a wide range by proper selection of the vulcanizing system. The usual practice is to use as fast a system as can be tolerated by the processing steps through which the material will pass without "scorching", that is, without premature vulcanization caused by heat during these processing steps. Rapid vulcanization affects economies by producing the largest volume of goods possible from the available equipment. This is particularly the case for products made in molds, because molds are costly, and their output is determined by the number of heats which can be made per day.

The rate of vulcanization increases exponentially with an increase in temperature; hence the tendency is to vulcanize at the highest temperature possible. In practice, this is limited by many factors, and the practical curing temperature range is 260 – 340°F (127 – 171°C). There are numerous exceptions both below and above this range, but it probably covers 95% of the products made.

Finishing operations following vulcanization include removal of mold flash, sometimes cutting or punching size, cleaning, inspection for defects, addition of fittings such as valves or couplings, painting or varnishing, and packing.

II.7 Peroxide Vulcanization

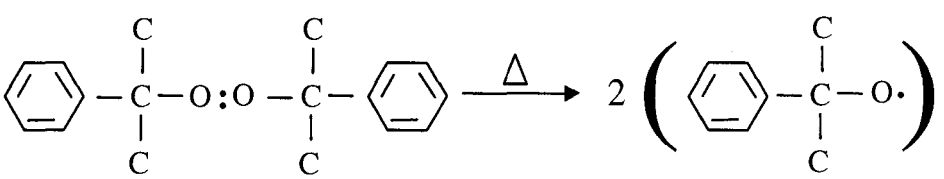
Peroxide vulcanization of rubber dates back to about 1914. Rubber was cured with benzoyl peroxide. However, except for limited use with silicones, this peroxide has not found a place in rubber vulcanization. Then, about 1950, di-tertiary butyl peroxide was found to give much better quality rubber vulcanizates than benzoyl peroxides. This peroxide was so volatile; however, that extreme care was required even in laboratory compounding to avoid excessive loss of peroxide during curing. Shortly thereafter,

dicumyl peroxide (Hercules Di- cup®) was found to have a good combination of physical and chemical properties for the compounding and curing of rubber.

Other peroxides are now available so that the rubber compounder may choose peroxide which gives a faster cure or one that may be used in compounds processed at higher temperatures. Among the peroxides available, however, an improvement in either of these two properties may be obtained only by a corresponding sacrifice of the other. That is, processability at higher temperatures is obtainable only with peroxides which are slower curing at a given temperature. Although the decomposition products from the cross-linking agent depend on the peroxide used, the mechanism as related to the elastomer is essentially the same.

II.7.1 Mechanism:

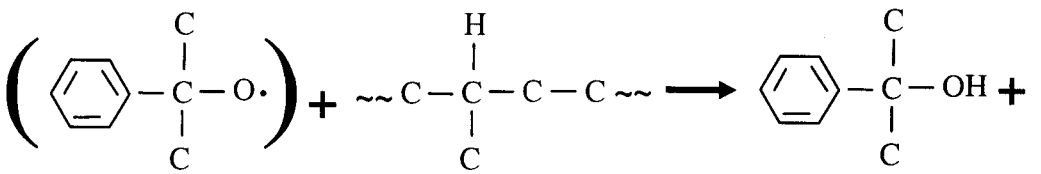
In the absence of other additives, peroxide vulcanization consists almost exclusively of creating carbon – to – carbon bonds between the polymer chains. That is, the peroxide itself does not become a part of the cross-link in the polymer. The following reaction shows how a typical peroxide used in rubber vulcanization decomposes to form free radicals which cause cross-linking.

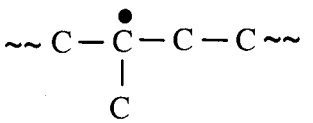


Homolytic Cleavage of Peroxide

First the dicumyl peroxide undergoes a homolytic cleavage producing cumyloxy radicals. Some of the cumyloxy radicals then abstract active unsaturated hydrogens from the polymer, producing polymer radicals which ultimately couple through carbon-carbon

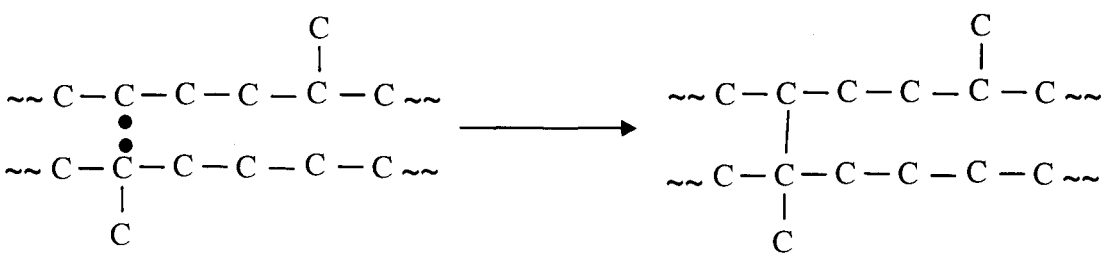
bonds to produce a cross-linked form of the polymer. The remaining cumyloxy radicals decompose to acetophenone and methyl radicals. These methyl radicals also can abstract hydrogens from the polymer.





Polymer Radical Formation

The principal reaction products of dicumyl peroxide are cumyl alcohol, acetophenone, and methane. The coupling reaction which occurs during peroxide vulcanization of polymers is shown below:



Although many other radicals probably can and do form, the important reaction of the radicals is coupling, as shown. The carbon – to - carbon coupling mechanism shown probably accounts for the increased oxidation stability of peroxide – cured rubber compared with sulfur – cured unsaturated polymers. Sulfur crosslinks are reported to be more sensitive to oxygen than are carbon – to – carbon bonds even in the age-resistant rubber products resulting from vulcanization with thiuram accelerators.

CHAPTER III

EQUIPMENT AND PROCEDURES

III. 1 Introduction

The unique properties of elastomers require special adaptations of the standard mechanical properties tests. The extent of elongation at failure, which directly relates to desirable elastomeric characteristics, is frequently a very useful performance parameter. The extent of elongation also gives an indication of the quality and degree of polymeric cross-linking (vulcanization). All the testing methodologies used for the project are adopted from the standard procedures of American Society for Testing and Materials (ASTM).

III. 2 Accelerated Testing

The time rate of chloramine–induced degradation of elastomers is controlled by both temperature and concentration levels. The acceleration study systematically varied these components and performed surface roughness, tensile strength, elongation and hardness tests to quantify the degradation. It was understood from the past research that exposure to nominal chlorine/chloramine concentrations of distribution systems would not produce meaningful differences in the performance characteristics of the elastomeric test materials. Therefore, an accelerated testing program using high-strength chlorine/chloramine solutions at elevated temperatures was devised.

III. 3 Testing Conditions

The ASTM procedure for accelerated elastomer degradation testing specifies a standard 70°C temperature and a 50ppm concentration for testing. While the ASTM protocols were followed for chloramines testing, the testing program was further explored by supplementing the ASTM test procedures to assess temperature and concentration effects. The standard ASTM test procedures were supplemented with additional accelerated degradation tests performed at temperature and chloramines concentration as defined in the following matrix.

Chloramine Concentration (PPM)	22°C	45°C	70°C
60	X	X	X
30	X	X	ASTM
1	X	X	X

Temperature

Table III.1 Matrix of testing conditions

Nine different exposure conditions served as the basis of the accelerated life-cycle testing program. These nine conditions were conveniently divided into 3 test programs, A, B and C as follows:

Task	Chloramine Concentrations	Temperatures
A	1 ppm	22°C, 45°C and 70°C
B	50 ppm	22°C, 45°C and 70°C
C	100 ppm	22°C, 45°C and 70°C

Table III.2 Description of tasks carried out and the conditions tested

Test solution conditions are checked daily by measuring the pH and chloramine concentration, and because chloramine is constantly consumed via reactions with the elastomeric materials, the solutions were drained and replaced every 24 hours. Each test program ran for 30 days. At the end of 3, 6, 12, 20 and 30 days the test coupons were removed from the test solutions and quantitatively assessed for degradation with the help of physical and chemical tests.

III. 4 Sample materials and test coupons

Molded rubber samples are obtained from Ashtabula Rubber Company for the purpose of the research. An agreement with Ashtabula Rubber Company was reached to supply EPDM elastomer formulations (composition presented in table III.3), based on a preliminary assessment of the elastomer variety in use and currently available to water distribution systems that will be used to represent "un-aged" conditions. These generally represent "R-Class" materials as defined by ASTM D2000. Elastomers from higher classifications (class M, Q and U) generally include specialty or propriety polymers and thus may or may not be representative of base materials. These materials where received in the form rectangular rubber slabs of size 6" x 7" x 0.80". These slabs are then cut into coupons according to the test protocol.

Test coupons were divided into two types based on the type of tests conducted on them. For tensile testing, the specimens were cut into a dumbbell shape and for hardness, change in mass and volume tests, they were cut into rectangles. These rectangles are removed on the test days for measurement and are replaced at the end of the testing. These are called the reusable samples. The tensile samples are strained to failure on the test day to measure the tensile properties.

Ingredient	PHR	Function
Nordel 1070	100	DuPont-1,2polybutadiene
FEF N550	100	Carbon black
Sun 22800 (or equiv.)	110	Extending oil
Sulphur	2	Primary vulcanizing agent
ZNO	5	Curing system additive (activator)
Stearic Acid	2	Curing system additive
Altax/Butyl Z/M Tuads	4.8	Accelerants

Table III.3 Composition of EPDM rubber material obtained from Ashtabula

The reusable samples were cut in 2" x 1" x .080" thick per ASTM D-3182. Tensile specimens were cut using a standard dumbbell specimen type C Die per ASTM D412. The specimen die cutting surface was carefully maintained because the cutting surface is required to ensure a smooth edge on the cut specimen. The shape of the tensile specimen avoided uneven breakage and the tendency to slide out of the testing grips. The narrow neck of the dumbbell specimen ensured a consistent breakage pattern, and the coupon's splayed ends gave substantially more grip area relative to the neck cross-section. Following ASTM procedures, the coupons were cut lengthwise along the grain (the direction of extrusion). Shown in figure III.1 is the typical dumbbell coupon dimensions:

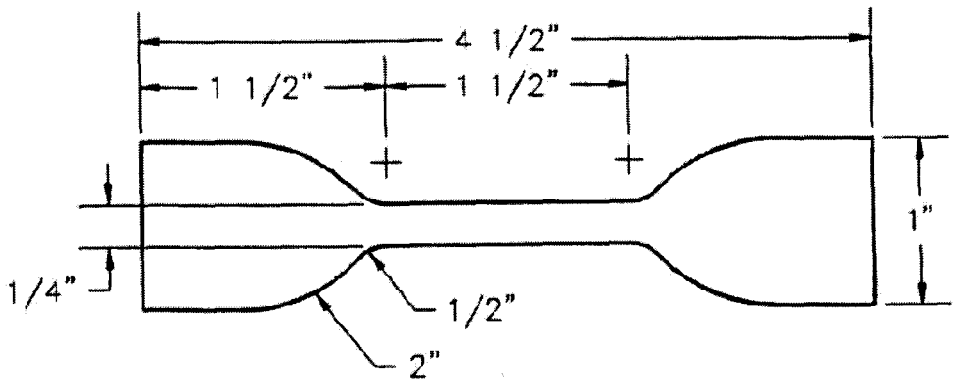


Figure III.1 Dimensions of the rubber coupon used for tensile testing

III. 5 Coupon Exposure Setup

Glass fixtures with spacers were used to suspend the coupons in solutions. The coupons were loaded onto the glass fixture and were placed in the test solution at the test temperature in a constant temperature circulating bath. This arrangement gave maximum exposure of rubber coupons to solution. Also, this design addressed a couple of serious concerns: first, the maintenance of equal fluid motion across the elastomer coupons and second, provision for ready inspection and removal of the coupons throughout the exposure sequence. A schematic representation of the setup is shown in figure III.2.

Each rubber type is placed in a stainless steel container with the chloramine test solution and the container is placed in the constant temperature circulating bath to maintain a constant temperature. A digital display on the front of the bath shows the temperature of the medium inside (figure III.5).

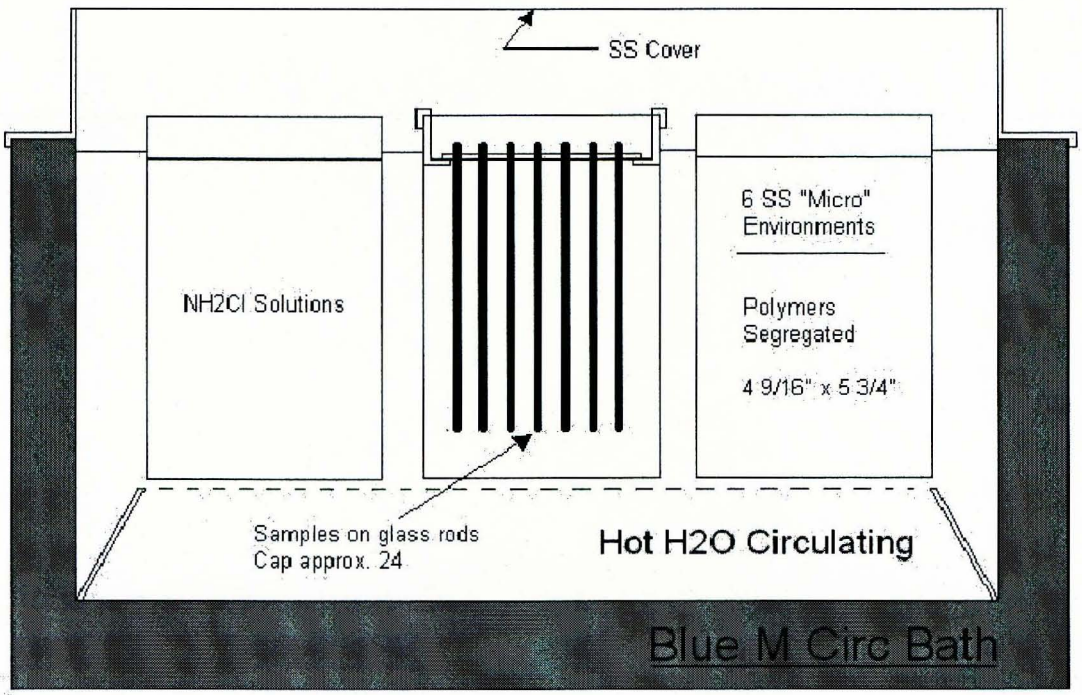


Figure III. 2 Schematic diagram of the hot water circulation bath

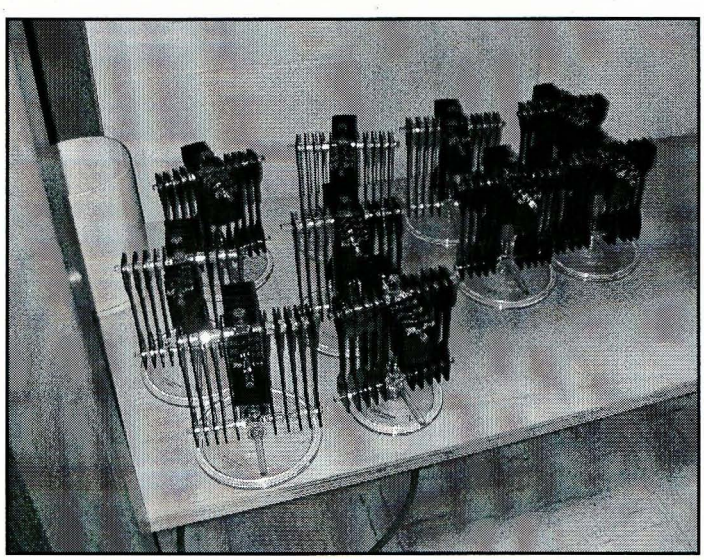


Figure III. 3 Glass fixtures loaded with rectangles and tensile samples

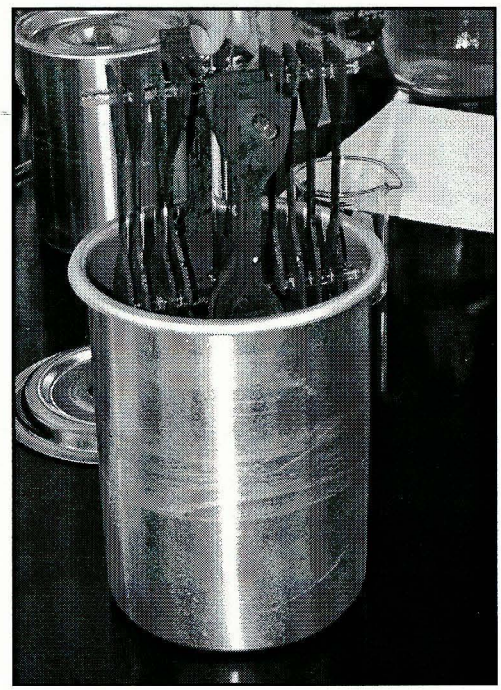


Figure III. 4 Glass fixture with loaded samples in a stainless steel container with chloramine test solution

Figure III. 5 Constant temperature circulating bath with digital temperature display on the front

III. 6 Preparation of the chloramine test solution

All the test solutions were prepared from the same de-ionized (DI) water having an initial resistivity of 18.3 Mega Ohms. Chlorine was added to the DI water in the form of sodium hypochlorite (NaOCl); ammonia was added as ammonium chloride. To provide uniform excess, chlorine and ammonium were added to the DI water in the ratio of 4 to 1 weight ratio of chlorine to ammonium. The pH adjustment was achieved by adding 7.0pH phosphate buffer to the chloramine solutions. The detailed procedure to prepare a 100ppm chloramine solution is given below:

1. 9.0 L of DI water is taken in a container for each of the three temperatures, 22C, 45C and 70C.
2. 36 mL of 7.0 pH phosphate buffer is added to the water.
3. NaOCl is added per the table below to the solution.
4. NH_4OH is added to the solution per the table below.
5. 18 – 20 mL of 7.0 pH buffer is added to the solution to bring down the pH to 8.3.

Temp °C	Avg. Conc.	Initial Conc.	7.0 pH Buffer/ L	NaOCl / L	NH_4OH/ L	7.0 pH Buffer/ L
70	60 ppm	120 ppm	4 ml	2.2ml	3.8 ml	2 – 8 ml
45	60ppm	90ppm	4 ml	1.7ml	2.7 ml	2 – 8 ml
22	60ppm	60ppm	4 ml	1.1 ml	1.8 ml	2 – 8 ml

Table III.4 Procedure to prepare chloramine solutions of different concentrations

III. 6.1 Checking the concentration of chloramine solution:

Chloramine concentration is determined by an amperometric titration utilizing phenylarsine oxide as the titrant. When the titrator cell is immersed in a sample

containing chlorine, current is generated. As phenylarsine oxide is added, the chlorine present as hypochlorite is reduced and the generation of current decreases proportionately due to the diminishing of the reducible species. When chlorine is present as chloramines, potassium iodide is added, releasing iodine which is titrated in a similar manner. The iodine content is calculated in terms of free chlorine. The instrument used is a Fisher CL Titrimeter Model 397. A detailed procedure is given below:

1. The electrode is rinsed prior to the titration using a wash bottle with DI water.
2. For a 100 ppm nominal solution, 2 ml of sample is added to 98 ml of DI water in the beaker provided with the instrument, for a total sample size of 100 ml. (used 25:1 dilution for 50 ppm solutions and no dilution for 1 ppm solutions)
3. To the diluted solution above, 1 ml of potassium iodide and 1 ml of 4.0 pH buffer are added, always in this order.
4. The electrode is lowered down into the solution and the instrument should be set for "Total" chlorine residual.
5. Using a pipette, phenylarsine oxide solution, the titrant is dispensed slowly and during the delivery the current in the watch meter decreases.
6. The end point will be noted when the addition of titrant causes no further change in the current. The pipette reading prior to the last delivery is used in the equation below to determine total chlorine residual in ppm.
7. Equation: Chlorine residual (ppm) = 200 D (A/V), where D = the dilution of the solution for the titration sample, A = ml of phenylarsine oxide solution required, and V = sample used in ml.

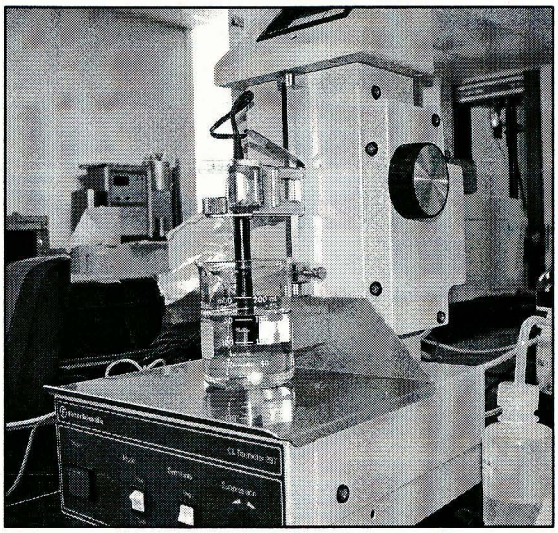


Figure III. 6 Chlorine Titrimeter with electrode dipped into the test solution

Freshly prepared chloramine solutions are then distributed into the stainless steel containers containing the glass fixtures loaded with rubber samples in each. These containers are then kept in the circulating baths to maintain temperature. The solutions are freshly prepared and replaced every 24 hours because chlorine is constantly consumed via reactions with the elastomeric materials and concentration drops considerably. These reactions on the elastomers consumed a substantial amount of the available chlorine (both free and combined) in the exposure solutions and usually altered solution pH as well. Significant variation in the chlorine exposure level and pH were unavoidable. To maintain the desired exposure conditions, it was necessary to monitor the baths daily, changing the solutions.

The chloramine levels were relatively stable and easier to maintain at 1ppm than at 50ppm or 100ppm. The daily fluctuations of 100ppm were as high as 70ppm and for 50ppm they were 20ppm. This rapid chloramine consumption foreshadowed the

reactivity of these species relative to elastomer degradation. The rapid depletion of the chloramines was indicative of the impact they exerted on the elastomeric materials.

III.7 Elastomer tensile properties testing methodology

The attack on elastomeric structures can proceed by at least two mechanisms. Depending on materials and vulcanization methods, the attack may concentrate on the polymeric cross-links formed during the vulcanization process, or, if the oxidant is powerful, it may actually rupture the polymeric backbone (in addition to the cross-links). In either case, the weakened structure manifests itself in a variety of ways: The surface may break across lines of tension, forming cracks that are visible to the naked eye; the tensile properties of the material may be significantly degraded; or the structure may lose its resilience and become embrittled. The loss of polymeric structural integrity may also contribute to water absorption and a physical swelling of the material. Such changes may alter shape and can be accompanied by a loss of the elastomeric fillers (released due to the breakdown of the polymer encapsulation).

Because elastomers are most commonly utilized for their flexure and shock dampening properties, the elastomeric tensile property of greatest concern to manufacturers is usually elongation (strain). The ultimate elongation at failure is typically a more useful tensile property than failure stress (ultimate load). Stress and strain are closely related properties and are both determined by the intrinsic qualities of the polymeric structure. Oxidant attack weakens this structure, bringing about profound changes in the elastomer's load-bearing capacity – the degradation of which is often as great as or greater than the impact on ultimate elongation.

Tensile strength was determined per ASTM D 412C. Coupons were tested to failure on a model 4505 Instron Universal Testing system with a 2603-80 balanced, long-travel elastomeric extensometer installed. The load cell is 1.0 kN – 224.8 lbs. The standard coupon elongation rate was set at 20 in. /min. Stress was determined based on the unloaded cross-sectional area of the coupon neck, and strain was calculated as percent of elongation along the neck of the coupon.

A brief procedure of tensile testing cycle is given below:

1. The dumbbell test coupons are removed from the test solution and are lightly blotted with lint free paper to remove moisture.
2. The Instron machine's mainframe power is turned on and the tensile sample is carefully inserted into the pneumatic clamps.
3. Extensometer is lowered and centered manually. The extensometer clip is positioned carefully establishing a gauge length required for testing.
4. The series IX automatic materials testing software is used to handle the remaining test. After entering the specimen and test parameters, the TEST icon from the main menu is clicked to start the test.
5. The end of the test is marked by sample failure. At the end, max stress, breaking strain (%), and 100% modulus will be printed out for each sample.

Tensile strength and ultimate elongation was measured and recorded at each test interval. This instrument is capable of collecting stress and strain data continuously during a test cycle. This data was used to calculate the crosslink densities, rate of deterioration of crosslink densities and the rate kinetics of the change, as presented in the chapter V.

CHAPTER IV

CONCEPTS OF RUBBER ELASTICITY

IV.1 Kinetic theory of Rubber elasticity

The behavior of rubbers when subjected to a static applied stress or strain shows that properties change significantly with both time of stressing or straining and with temperature. The implications of significant time and temperature dependence require that test conditions – rate, time, temperature and history of previous deformation – must be quoted if the results of a test are to be meaningful and applicable to the design of components.

The retractive force in stretched rubber is mainly due to entropy changes. Using this fact, it is possible to develop general expressions for the deformation of rubber units based upon the molecular structure of rubber. The derivations and the related background to the general expressions are commonly called the 'statistical theory', owing to the statistical treatment of the probable end-to-end distance of a typical single molecule; or alternatively the 'kinetic theory' owing to the analogy with the kinetic theory of gases, deriving from the consideration of thermal motions of molecular segments.

A typical rubber molecule consists of a long flexible chain of 10^4 - 10^6 units. With a large number of links the most probable end-to-end length is proportional to the square root of the number of links. This provides an explanation of the enormous extension

possible in soft rubber without rupture, since a chain of 10,000 units can elongate 10,000/100 times in going from its probable to its maximum length.

Thus for large deformations, the stress-strain curve is predicted by equation IV.1.

$$\sigma = nkT(\alpha - 1/\alpha^2) \qquad \text{(IV.1)}$$

Based on molecular (kinetic) theory, this equation predicts that a tensile stress-strain curve is nonlinear (Figure IV.1), with stress proportional to temperature. Smith (1962) further notes the same theory to develop equation (IV.2):

$$G = nkT = \rho RT/ M_c \qquad \text{(IV.2)}$$

where M_c equals molecular weight between cross links. This equation tells us an important fact that G (shear modulus) is directly related to M_c. This equation does further show the dependence of modulus on absolute temperature T. The other symbols used are: n, the number of molecular chains per unit volume; ρ the density; k, Boltzmann's constant; and R the gas constant.

Summarizing equations IV.1 and IV.2, in turn suggests the following equation IV.3:

$$\sigma = nRT\,[\alpha - 1/\alpha^2] \qquad \text{(IV.3)}$$

where the original length, L_0 , is increased to L ($\alpha = L/ L_0$), and RT is the gas constant times the absolute temperature. The quantity n represents the number of active network chain segments per unit volume. The quantity 'n' is equal to ρ/ M_c, and is defined in the equation (IV.2).

The "molecular" basis, primarily using thermodynamics, originally was referred to as the "statistical theory" by Gauss, and later referred to as the "Gaussian theory" by Kuhn (1936) and the "kinetic theory" by English researchers.

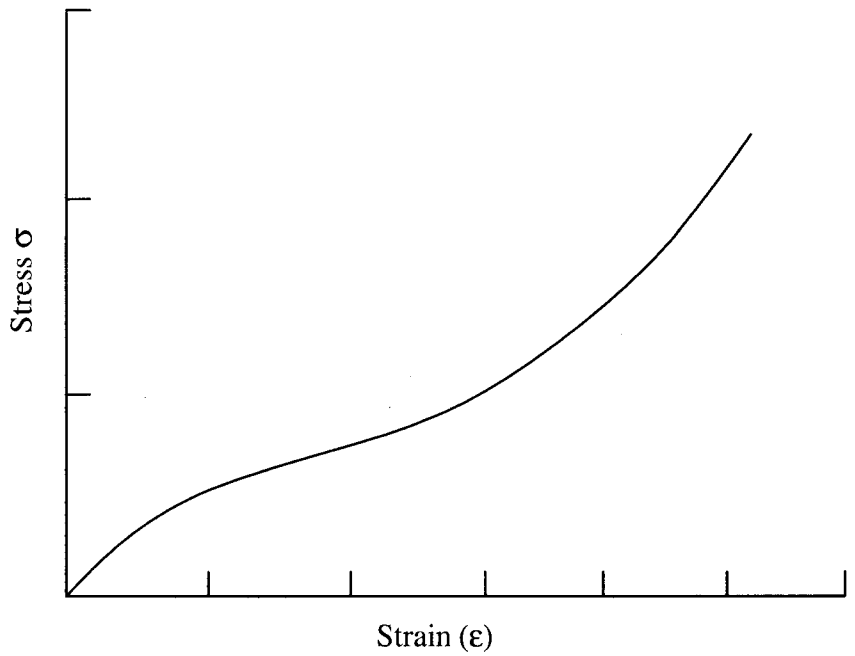


Figure IV.1 A stress-strain curve showing that equation IV.1 is nonlinear (Hertz, 1991).

IV.2 Activation energy

The activation energy is the threshold energy, or the energy that must be overcome in order for a chemical reaction to occur. Activation energy may otherwise be denoted as the minimum energy necessary for a specific chemical reaction to occur. The activation energy of a reaction is usually denoted by E_a. It was Arrhenius who first suggested that the temperature dependence of the specific reaction rate k, could be correlated with activation energy by an equation of the type,

$$k(T) = Ae^{-Ea/RT} \qquad \text{(IV.4)}$$

where k is the reaction rate constant; E_a the activation energy; R the gas constant; T the absolute temperature and A is a pre-exponential factor. Equation (IV.4), known as the Arrhenius equation, has been verified empirically to give the temperature behavior of most reaction rate constants within experimental accuracy over fairly large temperature ranges.

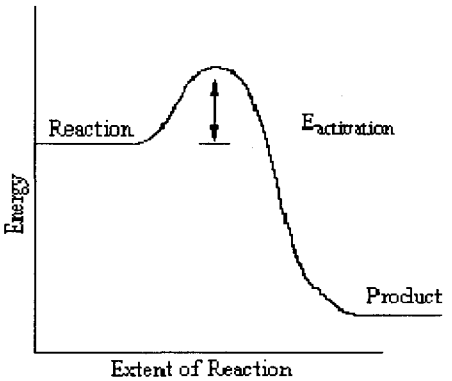


Figure IV.2 Extent of reaction and the significance of activation energy

The activation energy E_a has been equated with a minimum energy that must be possessed by reacting molecules before the reaction will occur. From the kinetic theory of gases, the factor $e^{-Ea/RT}$ gives the fraction of the collisions between molecules that together have this minimum energy *E*. The activation energy is determined experimentally by carrying out the reaction at several different temperatures. After taking the natural logarithm of equation (IV.4),

$$\ln k = \ln A - \frac{E}{R}\left(\frac{1}{T}\right) \qquad \text{(IV.5)}$$

it can be seen that a plot of ln k versus 1/T should be a straight line whose slope is proportional to the activation energy.

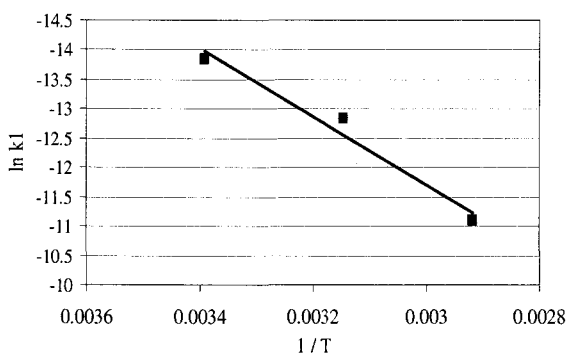


Figure IV.3 Sample Arrhenius plot in which the slope of the straight line represents (-E/R)

CHAPTER V

PERFORMANCE RESULTS AND DISCUSSION

After aging, the dumbbell shaped coupons were pulled in the Instron Universal Testing Machine with an extensometer to measure the tensile properties. In addition to ultimate stress and breaking strain, 100%, 300% and 500% modulus were also measured using the Instron. The measurements were taken on 0, 3, 6, 12, 20 and 30^{th} days during the 30-day aging period. The ultimate stress and breaking strain values were then used to calculate crosslink density n, using Gaussian theory of elasticity.

V.1 Gaussian Theory of Elasticity:

The Gaussian theory relating the stress-strain behavior of an elastomer to its crosslink density (from section IV.1) is given by,

$$\sigma = nRT (\alpha - 1/\alpha^2) \qquad \text{(From equation IV.3)}$$

Here, σ - Retractive Stress (Load / Initial Cross-sectional area)

α - Extension Ratio (Final length/ Initial length)

n - Active network chain segments per unit volume (Crosslink Density)

RT - Gas constant times the absolute temperature.

The following plot was generated by the Instron tensile testing machine and it shows that the experimental data follows the theoretical behavior (as in figure IV.1) predicted by equation IV.3.

Retractive stress is calculated by dividing the stress/load obtained from Instron with the cross-sectional area (0.02 sq. in) of the elastomer dumbbell coupon and

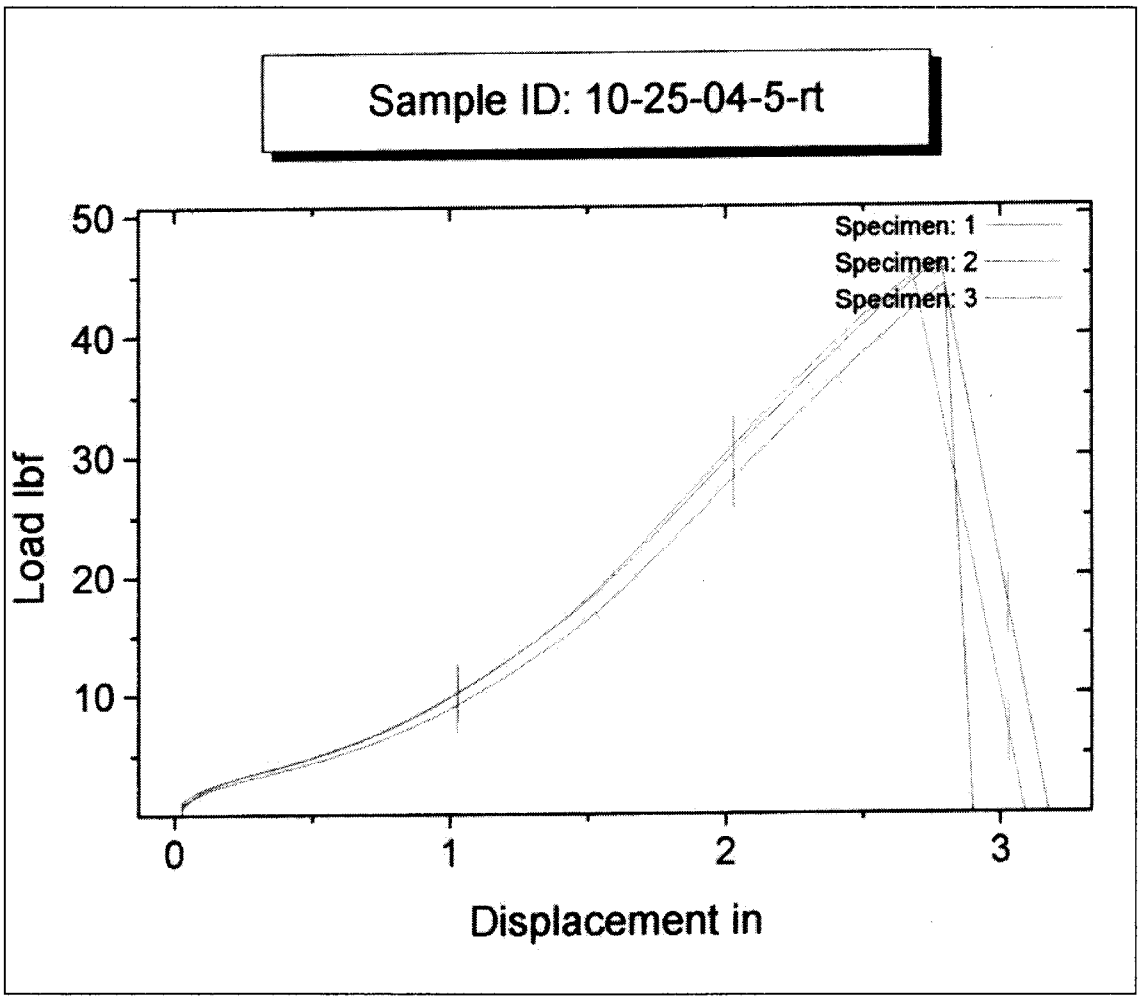


Figure V.1 Plot generated by Instron which matches the trend in figure IV.1

extension ratio is calculated from the strain data of the coupons with an initial length of 1.0 in. Crosslink density, n is calculated using the above values (step-wise calculations are presented in appendix II) and RT at three different temperatures and chloramine concentrations. The reproducibility of the data from the Instron was calculated prior to the experimentation and it is 0.06%. This error could be minimized by uniform clamping of the coupon with the jaws and calibrating the instrument before pulling a set of samples of each time interval.

Tables from V.1 through V.6 exhibit the results obtained from the above calculations.

Aging Time	Crosslink Density, Mol/CC		
	@ 22°C	@ 45°C	@ 70°C
0 Days	2.46E-03	2.46E-03	2.46E-03
12 Days	2.60E-03	2.61E-03	2.58E-03
20 Days	2.56E-03	2.55E-03	2.57E-03
30 Days	2.43E-03	2.44E-03	2.06E-03

Table V.1 Crosslink densities of EPDM-P, aged at 1ppm of chloramine concentration.

Aging Time	Crosslink Density, Mol/CC		
	@ 22°C	@ 45°C	@ 70°C
0 Days	2.46E-03	2.46E-03	2.46E-03
12 Days	2.45E-03	2.17E-03	1.42E-03
20 Days	2.35E-03	1.87E-03	1.35E-03
30 Days	2.32E-03	1.74E-03	1.28E-03

Table V.2 Crosslink densities of EPDM-P, aged at 30ppm of chloramine concentration.

Aging Time	Crosslink Density, Mol/CC		
	@ 22°C	@ 45°C	@ 70°C
0 Days	2.46E-03	2.46E-03	2.46E-03
12 Days	2.43E-03	2.09E-03	1.44E-03
20 Days	2.41E-03	1.89E-03	1.20E-03
30 Days	2.28E-03	1.63E-03	1.15E-03

Table V.3 Crosslink densities of EPDM-P, aged at 60ppm of chloramine concentration.

Aging Time	Crosslink Density, Mol/CC		
	@ 22°C	@ 45°C	@ 70°C
0 Days	1.77E-03	1.77E-03	1.77E-03
12 Days	1.86E-03	1.93E-03	2.12E-03
20 Days	1.94E-03	2.03E-03	2.38E-03
30 Days	1.99E-03	2.11E-03	2.45E-03

Table V.4 Crosslink densities of EPDM-S, aged at 1ppm of chloramine concentration.

Aging Time	Crosslink Density, Mol/CC		
	@ 22°C	@ 45°C	@ 70°C
0 Days	1.85E-03	1.85E-03	1.85E-03
12 Days	1.83E-03	1.81E-03	1.85E-03
20 Days	1.82E-03	1.77E-03	1.72E-03
30 Days	1.83E-03	1.70E-03	1.60E-03

Table V.5 Crosslink densities of EPDM-S, aged at 30ppm of chloramine concentration.

Aging Time	Crosslink Density, Mol/CC		
	@ 22°C	@ 45°C	@ 70°C
0 Days	1.77E-03	1.77E-03	1.77E-03
12 Days	1.77E-03	1.70E-03	1.66E-03
20 Days	1.74E-03	1.65E-03	1.49E-03
30 Days	1.73E-03	1.56E-03	1.43E-03

Table V.6 Crosslink densities of EPDM-S, aged at 60ppm of chloramine concentration.

Each of these calculated CLD values is the average of three CLDs of the three tensile samples. Standard deviations of these values are calculated and an example table is presented below. All the standard deviations are small, in the order of 10^{-5}.

	Crosslink Density, Mol/CC		
Aging Time	**@ 22°C**	**@ 45°C**	**@ 70°C**
0 Days	2.46E-03 (+/- 1.81E-05)	2.46E-03 (+/- 1.81E-05)	2.46E-03 (+/- 1.81E-05)
12 Days	2.43E-03 (+/- 4.55E-05)	2.09E-03 (+/- 9.67E-05)	1.44E-03 (+/- 3.38E-05)
20 Days	2.41E-03 (+/- 7.65E-05)	1.89E-03 (+/- 6.66E-05)	1.20E-03 (+/- 7.14E-05)
30 Days	2.28E-03 (+/- 1.50E-05)	1.63E-03 (+/- 7.13E-05)	1.15E-03 (+/- 2.32E-05)

Table V.6 (a) Standard deviations of the respective CLDs for EPDM – P aged at 60ppm of chloramine concentration.

Experimental data obtained from Instron is checked for its fit to the Gaussian theory. Based on the theory that the stress (σ) is linearly proportional to the factor ($\alpha - 1/\alpha^2$), experimental data is checked for linearity. Figure V.1 (a) is an example of the linearity check of Instron data. Every data cycle exhibited slight deviation in the initial stage due to the slack of dumbbell coupon and adjustment of speed of the moving jaws.

V.2 Rate of change of crosslink densities

The structure of a cross-linked elastomer may be idealized as the molecular structure in section II.7.1. The primary chains are cross-linked at many points along their length. The implication of a crosslink density of 1.77E-03 Mol/CC is that, there are 20-30 cross-links per primary molecule of molecular weight in the order of 1×10^5 g/mol. [The CLD values here are slightly higher than the values in literature, ~E-04 Mol/CC because these are pipe gaskets and seals and, as such, are harder than the rubber for other applications].

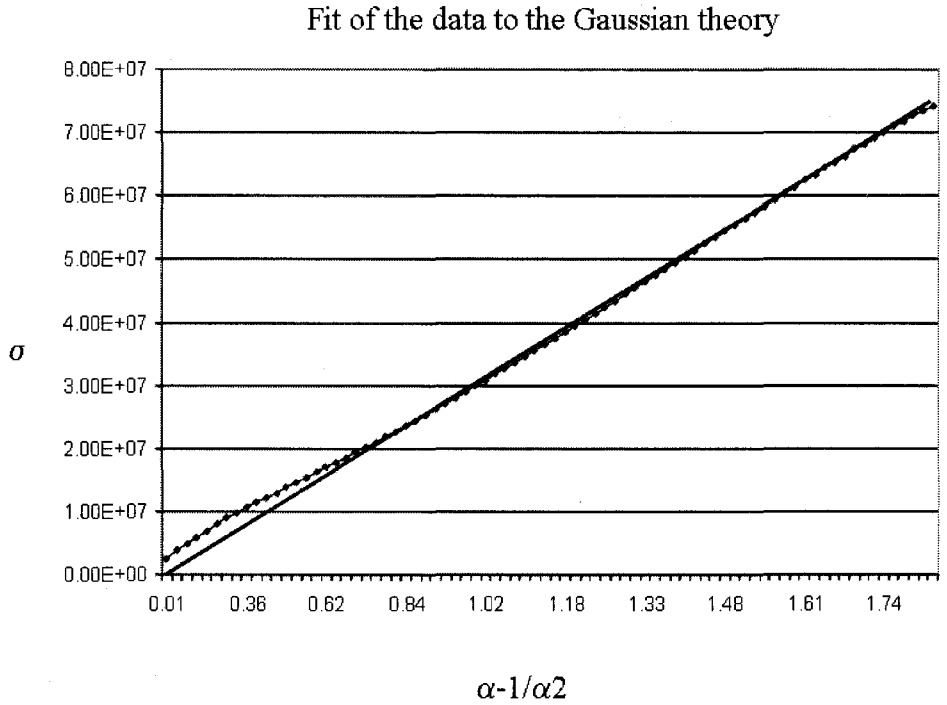


Figure V.1 (a) A plot of experimental data from Instron showing the linearity of the data

The crosslink densities (CLD) decreased over time and with increasing temperature during their aging. The rate of change of the property is calculated by determining the change in CLD over the time of aging (calculations are explained in appendix II). Tables V.7 and V.8 exhibit the rates calculated for EPDM-P and EPDM-S respectively.

Chloramine Concentration PPM	Rate of change of CLD, ΔCLD/ Day		
	@ 22°C	@ 45°C	@ 70°C
1	-8.919E-07	-1.01E-06	-1.1729E-05
30	-5.155E-06	-2.49E-05	-3.823E-05
60	-5.784E-06	-2.74E-05	-4.3639E-05

Table V.7 Rate of change of crosslink densities in 30 days for EPDM-P

Chloramine Concentration PPM	Rate of change of CLD, ΔCLD/ Day		
	@ 22°C	35 °C	@ 70°C
1	7.497E-06	1.164E-05	2.3493E-05
30	-4.718E-07	-4.977E-06	-8.608E-06
60	-1.448E-06	-6.976E-06	-1.209E-05

Table V.8 Rate of change of crosslink densities in 30 days for EPDM-S

The loss in crosslink densities of sulfur and peroxide cured EPDM rubber during chloramine aging followed common patterns. The rates of decrease were largest in the early stages of aging. To understand the underlying mechanism of deterioration, the rates are studied with respect to chloramine concentration at three temperatures. The plots of rate of change of CLD with respect to concentration are shown below.

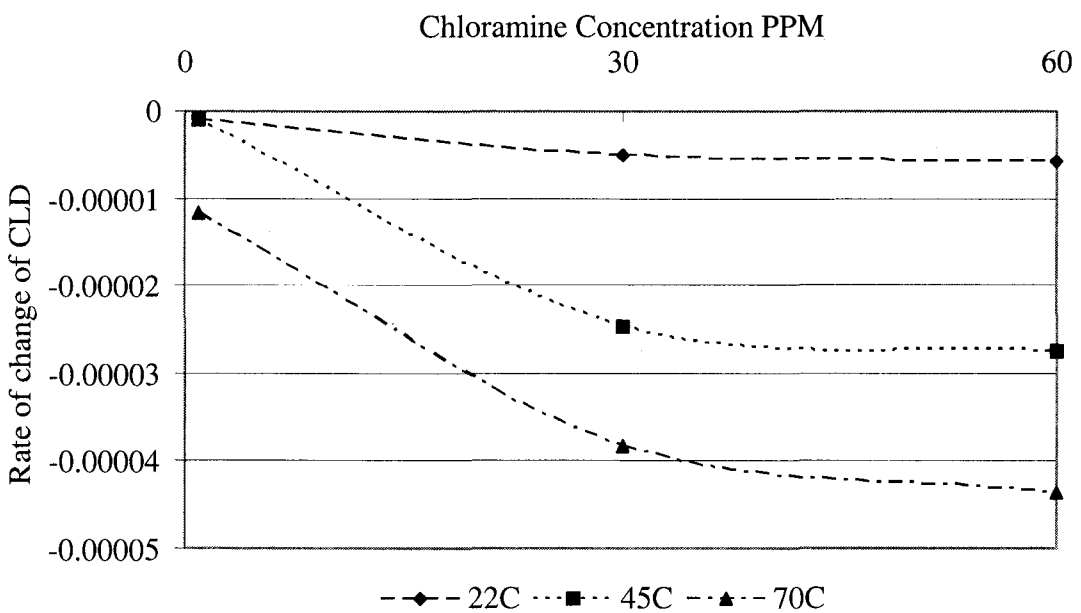


Chart V.1 Rate of change of CLD of EPDM - P with respect to chloramine concentration at three temperatures.

At 22°C, the deterioration rate is very low with a rate of 8.9 E-07 (mol/cm^3)/day or ΔCLD / Day. At 1ppm, the rates at 22°C and 45°C are very close when compared to the rate at 70°C i.e., 1.1729E-05 mol/cm^3/day. This trend exemplifies the effect of temperature on degradation of rubber properties. The 45°C and 70°C rate curves followed the same pattern; a large increase in the rate at low concentrations and a constant high rate at higher concentrations.

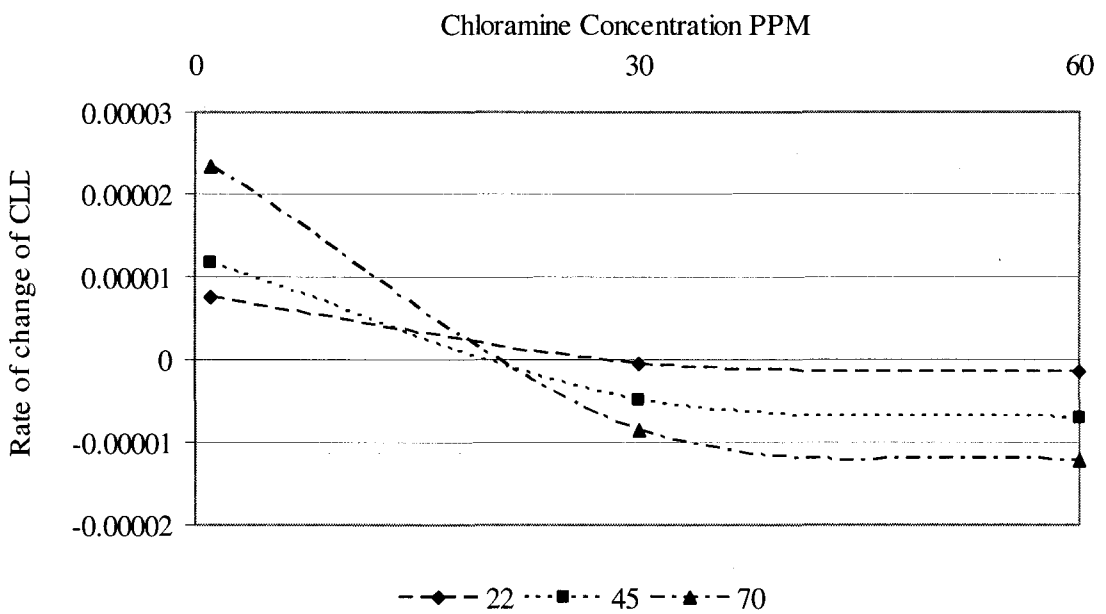


Chart V.2 Rate of change of CLD of EPDM - S with respect to chloramine concentration at three temperatures

At 1ppm, EPDM-S exhibited hardening or an increase in CLD, rather than a decrease in the property due to degradation. This could be due to formation of additional crosslinks within the molecule. According to the structure of vulcanized rubber, a link of two or more sulfur atoms are attached to the main chain. These extra sulfur atoms could break up with the main link and form additional links to other parts of the molecular chain. This process can result in the increase in CLD at lower concentrations, where the attacking chloramine is not sufficient enough to break the additional crosslinks. The

resulting hardening of the material was evident in other properties as well. Hardness was increased throughout the period of aging. This data is presented below in the chart V.3.

At high concentrations, the pattern of the rate of deterioration was similar to that of EPDM-P. The rate flattened at these high concentrations between 30ppm and 60ppm of chloramine. The greatest extent of hardening (at 1ppm) as well as deterioration (at 60ppm) occurred at 70°C.

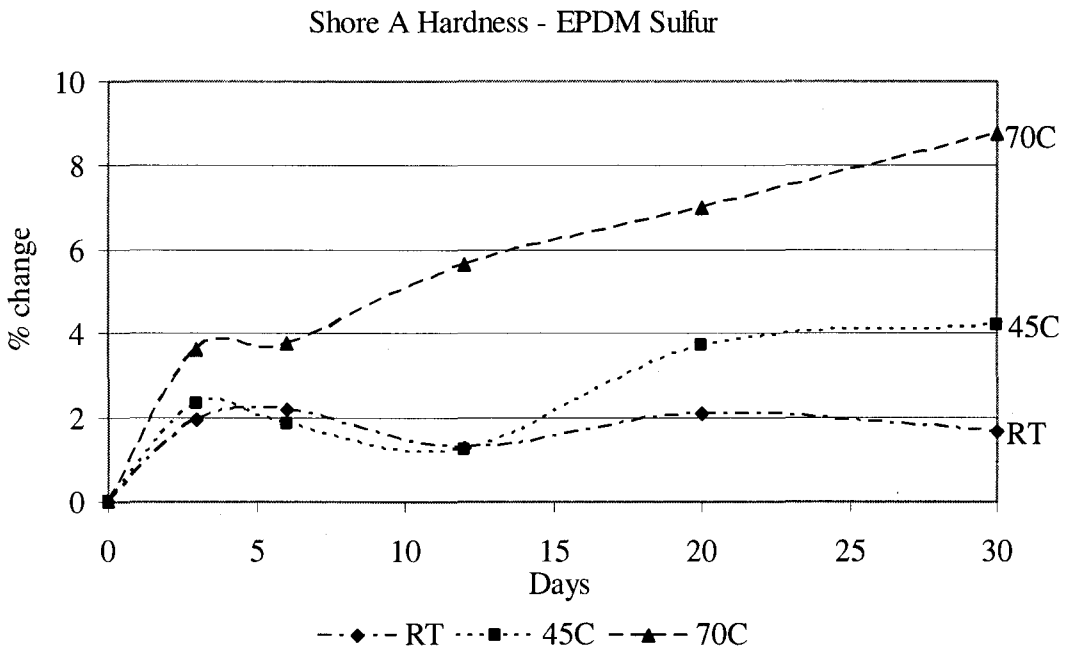


Chart V.3 Percent change of hardness of EPDM - S during the 30-day aging period at 1ppm chloramine concentration and three temperatures.

V. 3 Model of rate kinetics

Rate expressions were developed for both the EPDM rubbers to describe the observed deterioration of crosslink densities based on the data presented in tables V.7 and V.8. For EPDM - P, it is expressed in the equation below:

$$Rate = \frac{k_1 k_2 [C]}{k_1 [C] + k_2} \qquad (V.2)$$

Or,

$$Rate = \frac{1}{\frac{1}{k_1[C]} + \frac{1}{k_2}} \qquad \text{(V.3)}$$

The above rate equation suggests that the aging reaction is a two step process. At lower concentrations, the rate of reaction is a first order function of chloramine concentration, i.e. $k_1[C]$. At higher concentrations, the rate approaches zero order with a rate of k_2. It is understood that at these high concentrations the amount of chloramine present is abundant and the rate is no longer dependent on the concentration. Quantitatively, from equation V.3, when the value of $k_1[C]$ is high, $(1 / k_1[C])$ approaches zero and rate will be equal to k_2. Therefore, the course of reaction could be explained as a series of two reactions with k_1 being the rate constant for the first reaction and k_2 for the second reaction. When the rates at all the three temperatures are extrapolated to infinite concentration, the rates are equal to k_2 which are closer to the rates at 60ppm suggesting that rate approaches a constant value and becomes a zero order reaction. The values are presented in the table V.9 below:

Chloramine Concentration PPM	Rate of change of CLD, ΔCLD/ Day		
	@ 22°C	@ 45°C	@ 70°C
60	-5.78E-06	-2.74E-05	-4.36E-05
Infinity	-6.35E-06	-3.41E-05	-4.40E-05

Table V.9 Extrapolated reaction rates compared with those of 60ppm for EPDM - P

The developed model is checked for a best fit of data at all the three temperatures using nonlinear regression. The resulting r^2 values at 22°C, 45°C and 70°C were 0.99, 0.99 and 0.98 respectively. The rate constants in the equation were also estimated by this regression and are presented in the table V.10 below:

Temperature	Rate Constants	
	k_1	k_2
22°C	-9.81E-07	-6.35E-06
45°C	-2.68E-06	-3.41E-05
70°C	-1.53E-05	-4.40E-05

Table V.10 Rate constants of EPDM - P estimated by nonlinear regression

Deterioration of EPDM-S crosslink densities suggests a similar mechanism except the increase in CLD at 1ppm, as explained in section V.2. This increasing trend in crosslink densities at 1ppm introduces a new constant in the rate equation. The model is depicted in the equation below:

$$Rate = k_3 + \frac{k_1 k_2 [C]}{k_1 [C] + k_2} \qquad \text{(V.4)}$$

Or,

$$Rate = k_3 + \frac{1}{\frac{1}{k_1 [C]} + \frac{1}{k_2}} \qquad \text{(V.5)}$$

EPDM - S exhibited first order increase in the rate at lower concentrations, like EPDM - P. This change is quantified by the term $k_1[C]$ shown above in the equation V.5. At higher concentrations the rate was high but approached a constant value, behaving like a zero order reaction. The positive change in crosslink densities at 1ppm is quantified using a constant k_3. The increase in CLD pertains to the formation of additional cross links within the molecule. This increase is a zero order change with no dependence on chloramine concentration but depending on temperature.

The model was verified for best fit using nonlinear regression and the r^2 values are 0.999 at all the three temperatures. The three rate constants were also estimated by regression and are tabulated in the table V.11. Extrapolated rates were calculated with concentration approaching infinity. At infinity, the rates are equal to the sum of k_2 and k_3 at their respective temperatures. These values are close to the rates at 60ppm proving that the curve straightens and ultimately approaches a constant. These ultimate constants are presented in the table V.12 for comparison. In a physical point of view, k_1 represents the rate of loss of CLD per day and k_2 represents the rate of loss per day and per PPM of chloramine in the solution. Rate constants include everything that affects the reaction rate other than concentration, mainly temperature.

Temperature	Rate Constants		
	k_1	k_2	k_3
22°C	-1.68E-06	-1.16E-05	8.96E-06
45°C	-3.58E-06	-2.42E-05	1.48E-05
70°C	-7.86E-06	-4.65E-05	3.02E-05

Table V.11 Rate constants of EPDM - S estimated by regression

Chloramine Concentration PPM	Rate of change of CLD, ΔCLD/ Day		
	@ 22°C	@ 45°C	@ 70°C
60	-1.448E-06	-6.976E-06	-1.209E-05
Infinity	-2.65 E-06	-9.43 E-06	-1.63 E-05

Table V.12 Extrapolated reaction rates compared with those of 60ppm for EPDM - S

V.4 Temperature dependence of rate and activation energies

Arrhenius related the variation in reaction rate to temperature in a relationship as shown in equation V.6:

$$\ln k = -\left(E_a / RT\right) + \ln A \qquad \text{(V.6)}$$

where k is the reaction rate constant; E_a the activation energy; R the gas constant; T the absolute temperature and A is a pre-exponential factor. From this expression, the natural logarithm of reaction rate k is proportional to 1 / T, and the slope is equal to $-E_a / R$. As reaction rates at three temperatures are known, the activation energies, E_a were calculated for both the materials.

A modified version of the equation V.6 is used to predict the degradation rates and service lives at operating temperatures. The modified equation is presented as follows:

$$\frac{r_1}{r_2} = A \exp\left[-\frac{E_a}{RT}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right] \qquad \text{(V.7)}$$

where r_1 is the reaction rate at temperature T_1 etc., A is a constant and E_a is the activation energy.

At three temperatures 22°C, 45°C and 70°C, aging of EPDM - P has two reaction rate constants at each temperature and EPDM - S has three rate constants. Therefore, two activation energies are calculated for the two reaction steps for EPDM - P and three activation energies for EPDM -S. A linear regression of the Arrhenius equation in the form V.6 yielded the activation energy for a low chloramine concentration aging, E_{a1} = 48 kJ/mol and for high concentration aging, E_{a2} = 34 kJ/mol for EPDM - P. An Arrhenius

plot of EPDM - P rate constants of the low concentration process vs. 1 / T is presented in the chart V.4 as follows:

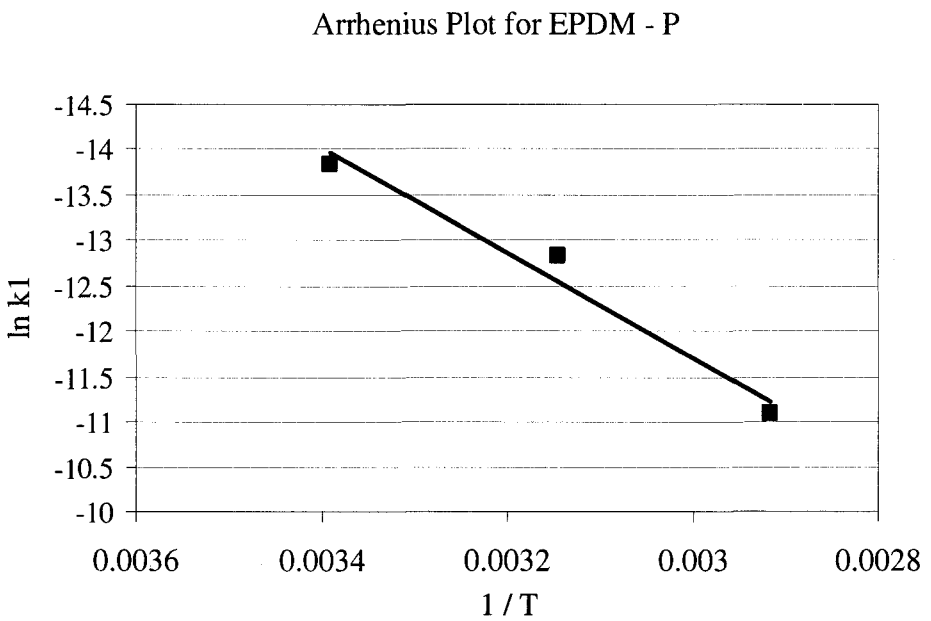


Chart V.4 Arrhenius plot of low concentration reaction rate constants vs. 1/T for EPDM - P

For EPDM - S, E_{a1} = 27 kJ/mol, E_{a2} = 24 kJ/mol and the activation energy for the process of additional cross linking at 1ppm, E_{a3} = 21 kJ/mol. All the E_a values, pre-exponential factors and R^2 values are tabulated in the tables V.13 and V.14 for EPDM – P and EPDM – S respectively. The low activation energies of EPDM - S suggests that EPDM - P has better resistance for chloramine aging than EPDM - S. These activation energies of EPDM rubber are slightly lower than the values in literature [6, 7] for similar type of rubber compounds obtained by various methods. Activation energies of Natural rubber compounds for aging in sea water were in the range of 55 - 65 kJ/mol. Analyses based on air aging yielded higher values, in the range of 86 - 94 kJ/mol. During heat

aging of EPDM membranes from 116°C to 150°C, activation energies for property changes ranged from 89 - 102 kJ/mol.

The following chart is the Arrhenius plot for the low concentration reaction process for EPDM - S:

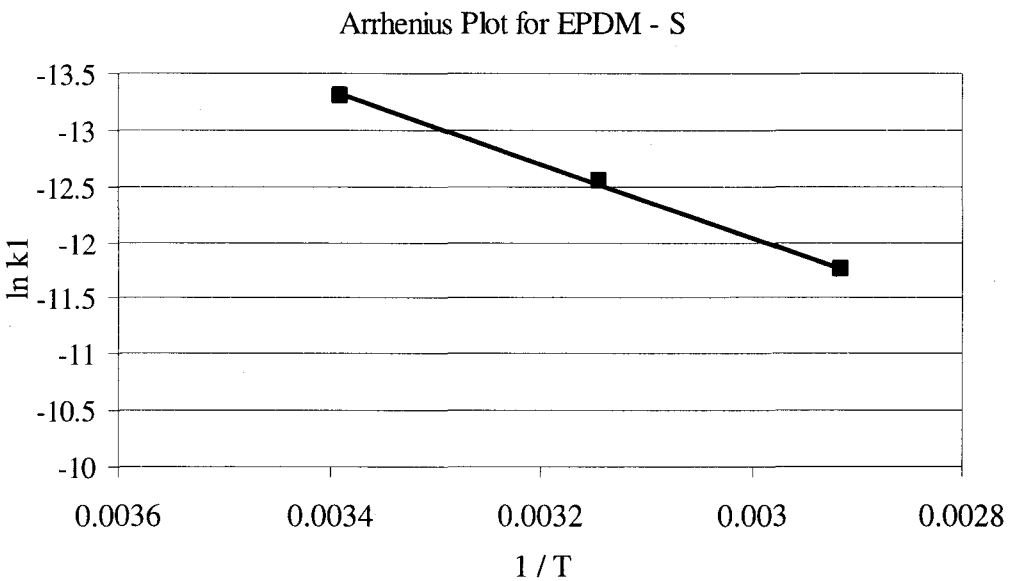


Chart V.5 Arrhenius plot of low concentration reaction rate constants vs. 1/T for EPDM – S

For EPDM – S, linear regression of ln k vs. 1/T yielded the activation energies with high R^2 values of 0.98 to 0.99 when compared to EPDM – P for which the R^2 values are 0.86 and 0.97. The frequency factors or pre-exponential factors are higher for EPDM- P than EPDM – S (tables V.13 and V.14). A value of 264.9 for the frequency factor of EPDM – P indicates that the number of collisions between the reactants which have the correct orientation to form products is high when compared to 0.102 for EPDM – S. Also, the frequency factor of the first reaction step in the series is higher than the one for second step which suggests that at lower concentrations, the collision of reactants is greater than at higher concentrations.

The activation energies (E_a), frequency factors (A) and the respective r^2 values of both the materials are reported below in the table V.13 and V.14:

	E_a KJ/Mol	A	R^2
k_1	47.9	264	0.97
k_2	34.2	8.92	0.86

Table V.13 The E_a, A and R^2 values of both the reaction steps for EPDM –P.

	E_a KJ/Mol	A	R^2
k_1	27.1	0.10	1.00
k_2	24.3	0.24	1.00
k_3	21.2	0.05	0.98

Table V.14 The E_a, A and R^2 values of the reaction steps for EPDM –S.

V.5 Prediction of service life

With the help of activation energies and rate constants, service life or the time taken for the material to lose a particular amount of crosslink density can be determined. A sample calculation is presented below:

Material: EPDM-P

Service conditions: Temperature – 24C, Chloramine concentration – 1ppm

% Deterioration in CLD at which the field part fails – 60%

Initial CLD: 2.46 x 10-3 Mol/cm3

With T = 297 K (24C)

k_1 =9.80E-07, k_2 = 8.68E-06

With [C] = 1ppm

Rate = 8.81E-07 mol/cm3.day

Life = (0.6 * 2.46E-03) / (8.81E-07)

= 1476 Days = 4 years

This service time represents a material which is fully and continuously exposed to chloramine unlike the field parts. Also the ratio of exposed surface area to volume of experimental coupon is very high when compared to the field parts, which gives a shorter life span for the laboratory samples. Using a geometric factor of the elastomeric part shape and surface area, a more precise service life could be calculated. Also, the same kind of calculation cannot be performed for EPDM-S due to the positive change in CLD at concentrations below 15ppm.

V.6 Conclusions

The calculations and rate equations developed have provided useful insights into the degradation mode and mechanism of chloramine induced EPDM failure. The key conclusion here is that, the degradation process is a two step series reaction. The first step of the series has its reaction rate proportional to the chloramine concentration and also has higher activation energy (48 KJ/Mol vs. 34 KJ/Mol for EPDM –P and 27 KJ/Mol vs. 24 KJ/Mol for EPDM – S) than the second step for both the EPDMs. The second reaction which approaches a zero order reaction state has lower activation energy than the first reaction, suggesting that the first reaction is the limiting step in the aging process.

The activation energies of EPDM – P are almost double the activation energies of EPDM – S, which explains the reason behind the greater resistance of EPDM – P towards chloramine attack than EPDM – S, especially at lower concentrations. Additionally, these

activation energies explain the low changes in other properties like swelling and hardness in EPDM – P when compared to EPDM – S or other rubber materials.

Accelerated aging experiments can provide useful insights into the aging phenomenon in a feasible time scale. Modeling of the change in crosslink density data and applying Arrhenius equation to the reaction rates aids in understanding the failure modes at a molecular level.

V.7 Recommendations

Based on the study conducted so far and the results obtained, the following recommendations were made to further investigate elastomer degradation:

1. A similar kind of calculations can be performed for SBR, Nitrile rubber, Natural rubber and Neoprene as well, to understand their failure modes as every rubber is compounded in a different way.
2. Insufficient data was the limitation for every similar study conducted in the past. Though there were three temperatures for the Arrhenius plot, another point of study between room temperature and 45°C would reinforce the results.
3. Aging of EPDM – S at 1ppm could be carried for a longer time, which is for an additional 60 days, to understand the extent of additional cross linking.

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APPENDIX I

NOMENCLATURE

E_a	–	Activation Energy
A	–	Frequency factor or Pre-exponential factor
EPDM - S	–	Ethylene Propylene Diene Methylene rubber – sulfur cured
EPDM - P	–	Ethylene Propylene Diene Methylene rubber – peroxide cured
k	–	Reaction rate constant
D	–	Dilution of solution for titration sample for chlorine titrimeter
V	–	Sample used for titration in ml
A	–	Volume of phenylarsine oxide solution required for titration in ml.
σ	–	Retractive Stress (Load / Initial Cross-sectional area)
α	–	Extension Ratio (Final length/ Initial length)
n or CLD	–	Active network chain segments per unit volume (Crosslink Density,)
R	–	Universal gas constant
T	–	Absolute temperature in °K
[C]	–	Chloramine concentration in ppm

Appendix II

SAMPLE CALCULATIONS

I. Data from Instron:

Data generated by the Instron tensile testing machine is presented in column 1 as 'Displacement' and in column 4 as 'Stress'.

Displacement (mm)	L = Dis + 25.4	α = L/25.4	Stress (Mpa)	Stress (dynes/cm2)	α - α ^2
0.3146	25.7146	1.01	0.7775	7.77E+06	0.04
0.7264	26.1264	1.03	0.8402	8.40E+06	0.08
1.1290	26.5290	1.04	0.8964	8.96E+06	0.13
1.5311	26.9311	1.06	0.9500	9.50E+06	0.17
1.9615	27.3615	1.08	1.0012	1.00E+07	0.22
2.3935	27.7935	1.09	1.0497	1.05E+07	0.26
2.8229	28.2229	1.11	1.1009	1.10E+07	0.30
3.2381	28.6381	1.13	1.1485	1.15E+07	0.34
3.6600	29.0600	1.14	1.1909	1.19E+07	0.38
4.0705	29.4705	1.16	1.2349	1.23E+07	0.42
4.5134	29.9134	1.18	1.2750	1.27E+07	0.46
4.9238	30.3238	1.19	1.3184	1.32E+07	0.49
5.3480	30.7480	1.21	1.3602	1.36E+07	0.53
5.7693	31.1693	1.23	1.4033	1.40E+07	0.56
6.1826	31.5826	1.24	1.4496	1.45E+07	0.60
6.6080	32.0080	1.26	1.4880	1.49E+07	0.63
7.0107	32.4107	1.28	1.5334	1.53E+07	0.66
7.4013	32.8013	1.29	1.5715	1.57E+07	0.69
7.8114	33.2114	1.31	1.6133	1.61E+07	0.72
8.2182	33.6182	1.32	1.6547	1.65E+07	0.75
8.6005	34.0005	1.34	1.6981	1.70E+07	0.78
8.9967	34.3967	1.35	1.7443	1.74E+07	0.81
9.3859	34.7859	1.37	1.7899	1.79E+07	0.84
9.7714	35.1714	1.38	1.8370	1.84E+07	0.86

10.1457	35.5457	1.40	1.8785	1.88E+07	0.89
10.5485	35.9485	1.42	1.9200	1.92E+07	0.92
10.9259	36.3259	1.43	1.9654	1.97E+07	0.94
11.2816	36.6816	1.44	2.0155	2.02E+07	0.96
11.6482	37.0482	1.46	2.0663	2.07E+07	0.99
11.9966	37.3966	1.47	2.1183	2.12E+07	1.01
12.3568	37.7568	1.49	2.1699	2.17E+07	1.03
12.7250	38.1250	1.50	2.2193	2.22E+07	1.06
13.0807	38.4807	1.51	2.2713	2.27E+07	1.08
13.4343	38.8343	1.53	2.3242	2.32E+07	1.10
13.7964	39.1964	1.54	2.3753	2.38E+07	1.12
14.1394	39.5394	1.56	2.4330	2.43E+07	1.14
14.4887	39.8887	1.57	2.4906	2.49E+07	1.16
14.8380	40.2380	1.58	2.5491	2.55E+07	1.19
15.1930	40.5930	1.60	2.6063	2.61E+07	1.21
15.5381	40.9381	1.61	2.6649	2.66E+07	1.23
15.8671	41.2671	1.62	2.7281	2.73E+07	1.25
16.1968	41.5968	1.64	2.7892	2.79E+07	1.26
16.5347	41.9347	1.65	2.8489	2.85E+07	1.28
16.8653	42.2653	1.66	2.9112	2.91E+07	1.30
17.1951	42.5951	1.68	2.9775	2.98E+07	1.32
17.5118	42.9118	1.69	3.0429	3.04E+07	1.34
17.8558	43.2558	1.70	3.1095	3.11E+07	1.36
18.1679	43.5679	1.72	3.1758	3.18E+07	1.38
18.4744	43.8744	1.73	3.2439	3.24E+07	1.39
18.7820	44.1820	1.74	3.3095	3.31E+07	1.41
19.1156	44.5156	1.75	3.3801	3.38E+07	1.43
19.4241	44.8241	1.76	3.4543	3.45E+07	1.44
19.7357	45.1357	1.78	3.5250	3.53E+07	1.46
20.0614	45.4614	1.79	3.5934	3.59E+07	1.48
20.3649	45.7649	1.80	3.6652	3.67E+07	1.49
20.6696	46.0696	1.81	3.7413	3.74E+07	1.51
20.9909	46.3909	1.83	3.8114	3.81E+07	1.53
21.2811	46.6811	1.84	3.8878	3.89E+07	1.54
21.6043	47.0043	1.85	3.9655	3.97E+07	1.56
21.9118	47.3118	1.86	4.0454	4.05E+07	1.57
22.2105	47.6105	1.87	4.1237	4.12E+07	1.59
22.5120	47.9120	1.89	4.2003	4.20E+07	1.61
22.8273	48.2273	1.90	4.2762	4.28E+07	1.62

23.1239	48.5239	1.91	4.3589	4.36E+07	1.64
23.4177	48.8177	1.92	4.4382	4.44E+07	1.65
23.7191	49.1191	1.93	4.5176	4.52E+07	1.67
24.0061	49.4061	1.95	4.6002	4.60E+07	1.68
24.2912	49.6912	1.96	4.6873	4.69E+07	1.70
24.6005	50.0005	1.97	4.7696	4.77E+07	1.71
24.8967	50.2967	1.98	4.8473	4.85E+07	1.73
25.2073	50.6073	1.99	4.9342	4.93E+07	1.74
25.5069	50.9069	2.00	5.0187	5.02E+07	1.76
25.8008	51.2008	2.02	5.1031	5.10E+07	1.77
26.0831	51.4831	2.03	5.1966	5.20E+07	1.78
26.3965	51.7965	2.04	5.2787	5.28E+07	1.80
26.6755	52.0755	2.05	5.3647	5.36E+07	1.81
26.9740	52.3740	2.06	5.4542	5.45E+07	1.83
27.2624	52.6624	2.07	5.5456	5.55E+07	1.84
27.5470	52.9470	2.08	5.6339	5.63E+07	1.85
27.8310	53.2310	2.10	5.7211	5.72E+07	1.87
28.1142	53.5142	2.11	5.8086	5.81E+07	1.88
28.3962	53.7962	2.12	5.8998	5.90E+07	1.90
28.6737	54.0737	2.13	5.9951	6.00E+07	1.91
28.9544	54.3544	2.14	6.0824	6.08E+07	1.92
29.2305	54.6305	2.15	6.1755	6.18E+07	1.93
29.5246	54.9246	2.16	6.2662	6.27E+07	1.95
29.8128	55.2128	2.17	6.3638	6.36E+07	1.96
30.0958	55.4958	2.18	6.4594	6.46E+07	1.98
30.3667	55.7667	2.20	6.5466	6.55E+07	1.99
30.6552	56.0552	2.21	6.6413	6.64E+07	2.00
30.9379	56.3379	2.22	6.7394	6.74E+07	2.01
31.2172	56.6172	2.23	6.8369	6.84E+07	2.03
31.5139	56.9139	2.24	6.9313	6.93E+07	2.04
31.7994	57.1994	2.25	7.0254	7.03E+07	2.05
32.0889	57.4889	2.26	7.1230	7.12E+07	2.07
32.3834	57.7834	2.27	7.2239	7.22E+07	2.08
32.6729	58.0729	2.29	7.3188	7.32E+07	2.10
32.9842	58.3842	2.30	7.4129	7.41E+07	2.11
33.2678	58.6678	2.31	7.5140	7.51E+07	2.12
33.5610	58.9610	2.32	7.6155	7.62E+07	2.14
33.8579	59.2579	2.33	7.7160	7.72E+07	2.15
34.1493	59.5493	2.34	7.8102	7.81E+07	2.16

34.4526	59.8526	2.36	7.9041	7.90E+07	2.18
34.7321	60.1321	2.37	8.0100	8.01E+07	2.19
35.0394	60.4394	2.38	8.1046	8.10E+07	2.20
35.3195	60.7195	2.39	8.2037	8.20E+07	2.22
35.6196	61.0196	2.40	8.3037	8.30E+07	2.23
35.9055	61.3055	2.41	8.4047	8.40E+07	2.24
36.1799	61.5799	2.42	8.5002	8.50E+07	2.25
36.4718	61.8718	2.44	8.6014	8.60E+07	2.27
36.7625	62.1625	2.45	8.7018	8.70E+07	2.28
37.0401	62.4401	2.46	8.8054	8.81E+07	2.29
37.3294	62.7294	2.47	8.8999	8.90E+07	2.31
37.6204	63.0204	2.48	9.0028	9.00E+07	2.32
37.9336	63.3336	2.49	9.1058	9.11E+07	2.33
38.2209	63.6209	2.50	9.2017	9.20E+07	2.35
38.4935	63.8935	2.52	9.3020	9.30E+07	2.36
38.7976	64.1976	2.53	9.4096	9.41E+07	2.37
39.0981	64.4981	2.54	9.5068	9.51E+07	2.38
39.3958	64.7958	2.55	9.6096	9.61E+07	2.40
39.7101	65.1101	2.56	9.7113	9.71E+07	2.41
39.9949	65.3949	2.57	9.8181	9.82E+07	2.42
40.3017	65.7017	2.59	9.9227	9.92E+07	2.44
40.6045	66.0045	2.60	10.0240	1.00E+08	2.45
40.9046	66.3046	2.61	10.1288	1.01E+08	2.46
41.2062	66.6062	2.62	10.2297	1.02E+08	2.48
41.5189	66.9189	2.63	10.3332	1.03E+08	2.49
41.8277	67.2277	2.65	10.4366	1.04E+08	2.50
42.1439	67.5439	2.66	10.5428	1.05E+08	2.52
42.4626	67.8626	2.67	10.6398	1.06E+08	2.53
42.7828	68.1828	2.68	10.7488	1.07E+08	2.55
43.0843	68.4843	2.70	10.8522	1.09E+08	2.56
43.3984	68.7984	2.71	10.9570	1.10E+08	2.57
43.7156	69.1156	2.72	11.0591	1.11E+08	2.59
44.0330	69.4330	2.73	11.1669	1.12E+08	2.60
44.3503	69.7503	2.75	11.2779	1.13E+08	2.61
44.6482	70.0482	2.76	11.3906	1.14E+08	2.63
44.9271	70.3271	2.77	11.5092	1.15E+08	2.64
45.2162	70.6162	2.78	11.6305	1.16E+08	2.65
45.4984	70.8984	2.79	11.7651	1.18E+08	2.66
45.7513	71.1513	2.80	11.9012	1.19E+08	2.67

46.0124	71.4124	2.81	12.0473	1.20E+08	2.69
46.1992	71.5992	2.82	12.1850	1.22E+08	2.69
46.4531	71.8531	2.83	12.3313	1.23E+08	2.70
46.6991	72.0991	2.84	12.4831	1.25E+08	2.71
46.9907	72.3907	2.85	12.6333	1.26E+08	2.73
47.2345	72.6345	2.86	12.7832	1.28E+08	2.74
47.4579	72.8579	2.87	12.9351	1.29E+08	2.75
47.7023	73.1023	2.88	13.0893	1.31E+08	2.76
47.9424	73.3424	2.89	13.2451	1.32E+08	2.77
48.1754	73.5754	2.90	13.3959	1.34E+08	2.78
48.4255	73.8255	2.91	13.5532	1.36E+08	2.79
48.6673	74.0673	2.92	13.7004	1.37E+08	2.80
48.9252	74.3252	2.93	13.8539	1.39E+08	2.81
49.1855	74.5855	2.94	14.0054	1.40E+08	2.82
49.4512	74.8512	2.95	14.1513	1.42E+08	2.83
49.7160	75.1160	2.96	14.3022	1.43E+08	2.84
49.9718	75.3718	2.97	14.4484	1.44E+08	2.85
50.2587	75.6587	2.98	14.5934	1.46E+08	2.87
50.5422	75.9422	2.99	14.7351	1.47E+08	2.88
50.8239	76.2239	3.00	14.8722	1.49E+08	2.89
51.1199	76.5199	3.01	15.0161	1.50E+08	2.90
51.4026	76.8026	3.02	15.1566	1.52E+08	2.91
51.7053	77.1053	3.04	15.3000	1.53E+08	2.93
51.9926	77.3926	3.05	15.4372	1.54E+08	2.94
52.2978	77.6978	3.06	15.5738	1.56E+08	2.95
52.6095	78.0095	3.07	15.7090	1.57E+08	2.97
52.9221	78.3221	3.08	15.8381	1.58E+08	2.98
53.2387	78.6387	3.10	15.9775	1.60E+08	2.99
53.5586	78.9586	3.11	16.1105	1.61E+08	3.01
53.8875	79.2875	3.12	16.2435	1.62E+08	3.02
54.2142	79.6142	3.13	16.3754	1.64E+08	3.03
54.5298	79.9298	3.15	16.5055	1.65E+08	3.05
54.8659	80.2659	3.16	16.6299	1.66E+08	3.06
55.1869	80.5869	3.17	16.7584	1.68E+08	3.07
55.5086	80.9086	3.19	16.8861	1.69E+08	3.09
55.8540	81.2540	3.20	17.0178	1.70E+08	3.10
56.1807	81.5807	3.21	17.1385	1.71E+08	3.11
56.5028	81.9028	3.22	17.2669	1.73E+08	3.13
56.8423	82.2423	3.24	17.3877	1.74E+08	3.14

57.1764	82.5764	3.25	17.5148	1.75E+08	3.16
57.4987	82.8987	3.26	17.6303	1.76E+08	3.17
57.8405	83.2405	3.28	17.7555	1.78E+08	3.18
58.1700	83.5700	3.29	17.8786	1.79E+08	3.20
58.5088	83.9088	3.30	17.9988	1.80E+08	3.21
58.8405	84.2405	3.32	18.1186	1.81E+08	3.23
59.1738	84.5738	3.33	18.2349	1.82E+08	3.24

Column 2: Final length of the coupon = Strained length + Initial length (25.4 mm)

E.g. L = 0.3146 + 25.4 = 25.7146 mm.

Column 3: Extension ratio, α = Final length / Initial Length

E.g. $\alpha = 25.7146 / 25.4 = 1.01$

Column 5: Converting Stress (σ) in MPa to Dynes/Cm^2 by multiplying with 10^7

E.g. 0.775 MPa = 7.75×10^6 Dynes/Cm^2

Column 6: $(\alpha - 1/\alpha^2)$ is calculated,

E.g. $(1.01 - 1/1.01^2) = 0.04$

II. Calculating Cross link density, N:

From the Gaussian theory, $\sigma = NRT(\alpha - 1/\alpha^2)$, slope of the line σ vs. $(\alpha - 1/\alpha^2)$ is equal to NRT, from which N is determined by dividing with RT.

E.g. Slope of σ vs. $(\alpha - 1/\alpha^2)$ = 5.96E+07 Dynes/Cm^2

$$\frac{5.96E+07}{(8.31E+07)\times 295} = 2.43E\text{-}03 \text{ Mol/Cm}^3$$

III. Calculation of rate of change in CLD:

At a particular concentration, CLDs at all the three temperatures and times are calculated. As a sample, the CLDs of EPDM – P at 22°C for all the four test days are presented below:

Time(Days)	@22°C	@45°C	@70°C
0	2.46E-03	2.46E-03	2.46E-03
12	***2.43E-03***	2.09E-03	1.44E-03
20	2.41E-03	1.89E-03	1.20E-03
30	2.28E-03	1.63E-03	1.15E-03

At each of the three temperatures, rate of change in CLDs is equal to the slopes of CLD with respect to time. These rates are calculated and are presented below:

Rate	-5.78E-06	-2.74E-05	-4.36E-05

Likewise, rates of change in CLDs are calculated at all the three concentrations. They are tabulated as follows:

Concentration (ppm)	22°C	45°C	70°C
1	-8.92E-07	-1.01E-06	-1.17E-05
30	-5.16E-06	-2.49E-05	-3.82E-05
60	-5.78E-06	-2.74E-05	-4.36E-05

IV. Regression and Rate Equation:

Using non-linear regression, the data is fit into a rate equation with the help of 'Polymath' software. For the data above, the following rate equation was fit with highest r^2 values.

$$Rate = \frac{k_1 k_2 [C]}{k_1 [C] + k_2}$$

A sample polymath report is shown below:

POLYMATH Report
Nonlinear Regression (L-M) 08-Mar-2006

Model: r22 = (k1*k2*C)/((k1*C) + k2)

Variable	Initial guess	Value	95% confidence
k1	1.0E-06	9.806E-07	1.486E-06
k2	0.0001	6.348E-06	1.871E-06

Nonlinear regression settings
Max # iterations = 64

Precision

R^2	0.9993547
R^2adj	0.9987094
Rmsd	3.187E-08
Variance	9.143E-15

General

Sample size	3
Model vars	2
Indep vars	1
Iterations	10

Source data points and calculated data points

	C	r22	r22 calc	Delta r22
1	1	0.0000008919	8.494E-07	4.25E-08
2	30	0.000005155	5.221E-06	-6.635E-08
3	60	0.000005784	5.73E-06	5.416E-08

The above report was generated for the 22°C reaction rates for EPDM – P. The same regression is carried out for 45°C and 70°C as well. Therefore, a rate equation and the respective rate constants are determined in this step.

V. Arrhenius equation and activation energy

Arrhenius rate equation,

$$\ln k = -\left(E_a/RT\right) + \ln A$$

is used to determine the activation energies of the processes. Natural logarithm of the rate constant vs. the inverse of absolute temperature yields a straight line for which the slope is equal to E_a/RT. The calculations are tabulated below:

Temperature	k1	k2	ln k1	ln k2	T (K)	1/T
22°C	9.81E-07	6.35E-06	-13.835	-11.967	295	0.00339
45°C	2.68E-06	3.41E-05	-12.83	-10.287	318	0.00314
70°C	1.53E-05	4.40E-05	-11.09	-10.032	343	0.00292

Slope of $\ln k_1$ vs. $1 / T = -5766.58$

$E_a = -5766.58 \times R = -5766.58 \times 0.008314 =$ **47.94 KJ / Mol**

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